Job No.: 1505-93197 Ref.: EP 0385426
Translated from German by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

EUROPEAN PATENT OFFICE
EUROPEAN PATENT NO. 0 385 426 A1

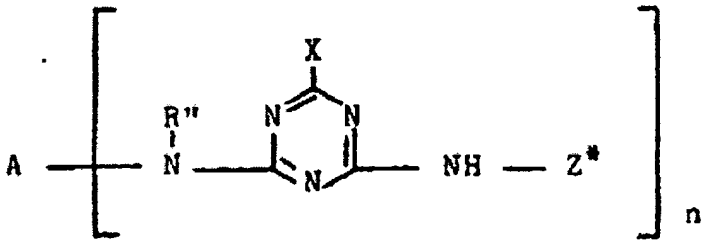
Int. Cl.[5]:	C 09 B 62/04 C 09 B 62/503 D 06 P 1/38
Filing No.:	90103874.5
Filing Date:	February 28, 1990
Publication Date of Application:	September 5, 1990 Patent Bulletin 90/36
Priority	
Date:	March 3, 1989
Country:	DE
No.:	3906778
Designated Contracting States:	CH, DE, FR, GB, IT, LI

WATER-SOLUBLE FIBER REACTIVE DYES, METHOD FOR PRODUCING THEM AND THEIR USE

Inventor: Dr. Reinhard Hähnle
Kastanlenweg 7a
D-6340 Königstein/Taunus (DE)

Applicant: Hoechst Aktiengesellschaft
Postfach 80 03 20
D-6230 Frankfurt am Main 80 (DE)

Dyes corresponding to the general formula



in which:

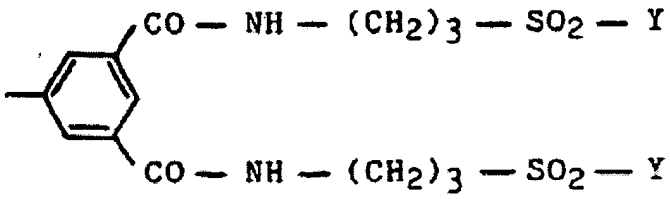
A is a residue of a dye, preferably a water-soluble sulfo group containing dye and preferably one from the azo series, of these especially the residue of a sulfo group containing monoazo or diazo dyes;

n is the number 1 or 2, preferably 1;

R" is a hydrogen atom or an alkyl group with 1-4 C atoms, such as the methyl group;

X is a chlorine or fluorine atom;

Z* is a group of the general formula



in which

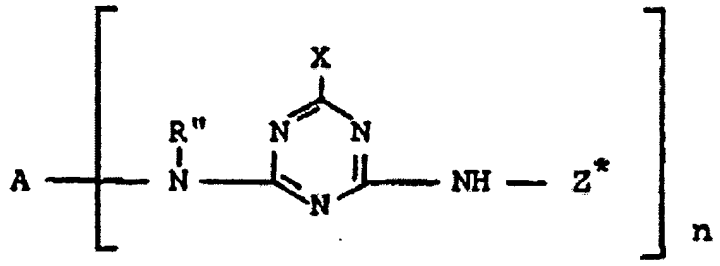
Y is the vinyl group or β-chloroethyl group or preferably the β-sulfatoethyl group.

The new dyes color carbonamide group and/or hydroxy group-containing materials such as synthetic polyamide fibers and wool and especially cellulose fiber materials like cotton, in brilliant, fast tones. They are characterized by high fiber-dye binding stability and afford dyeings and printings with high dye yield.

The invention concerns the industrial field of fiber reactive dyes.

The practice of dyeing with reactive dyes has recently led to increased requirements on the quality of dyeing and the economy of the dyeing process. As a consequence, there is additionally a need for new reactive dyes that have improved properties, especially with reference to fastness. For example, fiber reactive dyes are known from British Patent No. 1 576 237, European Patent Applications Nos. 0 070 806A, 0 070 808A and 0 221 013A and the German Patent Applications (Offenlegungsschrift) Nos. 33 27 641, 35 26 551 and 36 28 090; nevertheless, the task of this invention was to find new improved reactive dyes that dye cotton all shades. The new dyes should be characterized above all by high fiber-dye binding stability and should be particularly suitable for dyeing by the pad dyeing process; furthermore, the dye that does not become fixed on the fiber should be easily washed away. Furthermore, the dyeings obtainable with the new dyes must have good general fastness, for example good lightfastness and wetfastness.

With this invention this task was solved by finding the compounds of the general formula (1)



(1)

in which:

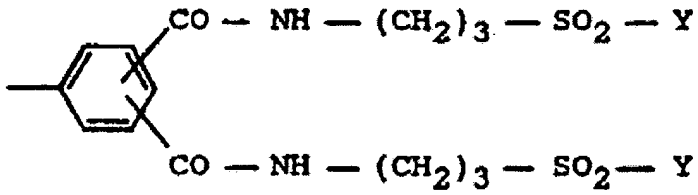
A is the residue of a sulfo group-containing dye, especially an azo dye or metal complex azo dye such as a sulfo group containing mono- or diazo dye or a sulfo group containing 1:1 copper complex-monoazo or diazo dye;

n is the number 1 or 2, preferably 1;

R" is a hydrogen atom or an alkyl group with 1-4 C atoms, such as the methyl group;

X is a chlorine or fluorine atom;

Z* is a group of the general formula



(2)

in which

Y is the vinyl group or the β-chloroethyl, β-phosphatoethyl or the β-acetyloxyethyl group or preferably the β-sulfatoethyl group.

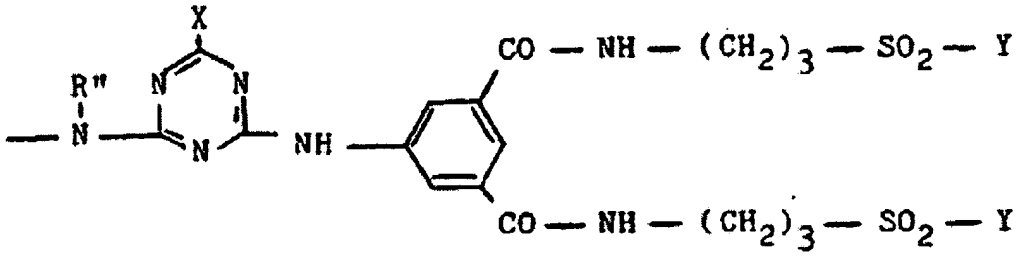
Dyes of general formula (1) that have a total of 1-6 sulfo groups are preferred. The dye residues A can additionally contain other conventional fiber reactive groups.

Dyes with residue A or the dyes underlying the compounds of general formula (1) with an amino group –NHR" are described in many places in the literature, for example in the applications and patents mentioned above, in the European Patent Application Publication No. 0 076 782A and further in Venkataraman, The Chemistry of Synthetic Dyes, New York, London, 1972, Volume VI, pp. 213-297.

Alkyl groups R" are, for example, n-butyl, n-propyl and ethyl groups, preferably methyl groups. Preferably, R" is a hydrogen atom.

The important azo dyes corresponding to general formula (1) are ones in which A is a residue of a dye of the benzoazonaphthol, benzoazo-1-phenyl-5-pyrazolone, benzene-azo-benzene, naphthaleneazobenzene, benzeneazoaminonaphthalene, naphthaleneazonaphthalene, naphthaleneazo-1-phenyl-5-pyrazolone, benzolazopyridone and naphthaleneazopyridone series, where also, the sulfo group-containing dyes are preferred.

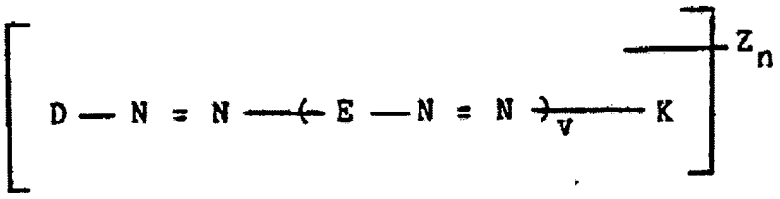
This invention thus concerns especially water-soluble sulfo group-containing azo dyes that contain the fiber reactive group Z of the general formula (3)



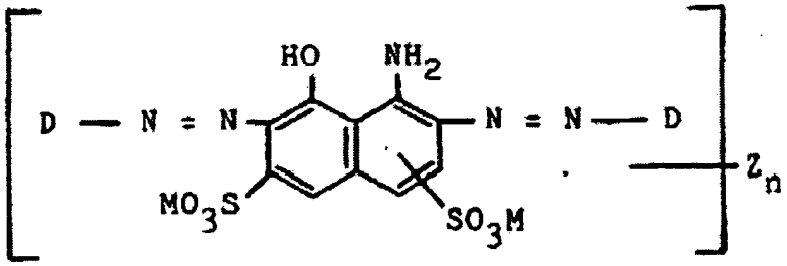
(3)

in which R", X and Y have the meanings given above, one or two times.

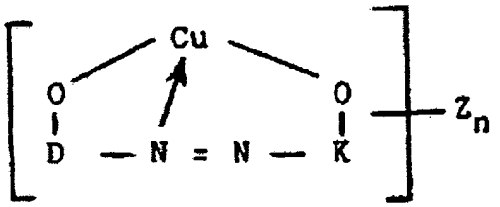
Such azo dyes of the general formula (I) are, for example, dyes of the general formulas (4a), (4b) and (4c)



(4a)



(4b)



(4c)

in which

M stands for a hydrogen atom or an alkali metal like sodium, potassium or lithium,

D in each case stands for the residue of a diazo component, which can be the same or different from each other,

E means the divalent residue of a compound capable of coupling and diazotization,

K is the residue of a coupling component,

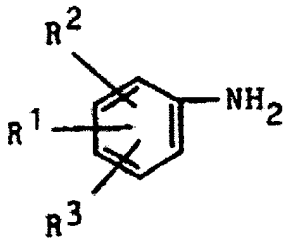
v stands for the number 0 or 1,

Z is a residue of general formula (3),

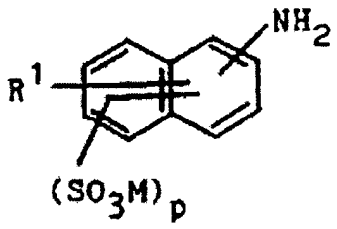
n is the number 1 or 2, preferably 1, and

the residue Z is linked to residue D or residue K or in the case n = 2 to D and K each or to both Ds.

Aromatic residues D of the diazo components D-NH_2 that do not carry any fiber reactive group of the general formula (3) are, for example, those of the amines of the general formulas (5a) and (5b)



(5a)



(5b)

in which

R^1 is a hydrogen atom, a sulfo group or a group of the general formula $-SO_2-Y$, with Y having the meaning given above,

R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms like acetyl and propionyl, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, cyano, carboxy, sulfo, alkanoylamino with 2-5 C atoms like acetylamino, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, nitro, sulfamoyl, N-(C_1-C_4 alkyl) sulfamoyl, alkylsulfonyl with 1-4 C atoms, phenylsulfonyl or phenoxy,

p means the number 0, 1 or 2 (where this group means a hydrogen atom if p is equal to zero) and

M has the meaning given above,

where the benzene or naphthalene linker can additionally contain a hydroxy group in ortho position to the NH_2 group.

R^2 here is preferably hydrogen, methyl, methoxy, bromine, chlorine, carboxy and sulfo, and R^3 is hydrogen, methyl, methoxy, chlorine, carboxy, sulfo and acetylamino.

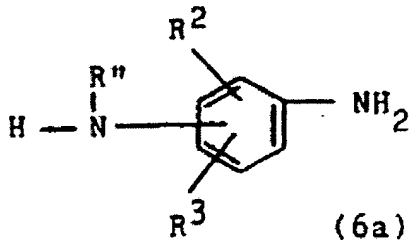
The substituents "sulfo," "carboxy," "phosphato" and "sulfato" include both their acid forms and their salt forms. Accordingly, sulfo groups mean groups corresponding to the general formula $-SO_3M$, carboxy groups mean groups in correspondence with the general formula –COOM, phosphato groups mean groups corresponding to the general formula $-OPO_3M_2$, and sulfato groups correspond to groups of the general formula $-OSO_3M$, in each case with M having the meaning given above.

Aromatic amines of the general formula $D\text{-}NH_2$ in correspondence with formulas (5a) and (5b) are, for example:

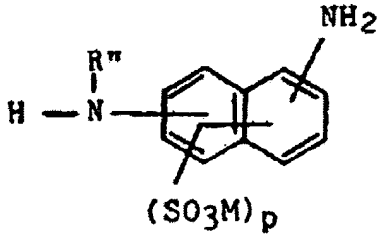
2-amino- or 4-aminobenzoic acid, 3-aminobenzoic acid, 3-chloroaniline-6-carboxylic acid, aniline-2- or -3- or -4-sulfonic acid, 2,5-disulfoaniline, 2,4-disulfoaniline, 3,5-disulfoaniline, 2-aminotoluene-4-sulfonic acid, 2-aminoanisol-4-sulfonic acid, 2-aminoanisol-5-sulfonic acid, 4-aminoanisol-2-sulfonic acid, 2-ethoxyaniline-5-sulfonic acid, 2-ethoxyaniline-4-sulfonic acid, 4-sulfo-2-aminobenzoic acid, 2,5-dimethoxyaniline-4-sulfonic acid, 2,4-dimethoxyaniline-5-sulfonic acid, 2-methoxy-5-methylaniline-4-sulfonic acid, 4-aminoanisol-3-sulfonic acid, 4-aminotoluene-3-sulfonic aid, 2-aminotoluene-5-sulfonic acid, 2-chloroaniline-4-sulfonic acid, 2-chloroaniline-5-sulfonic acid, 2-bromoaniline-4-sulfonic acid, 2,6-dichloroaniline-4-sulfonic acid, 2,6-dimethylaniline-3-sulfonic acid or -4-sulfonic acid, 3-acetylamino-6-sulfoaniline, 4-acetylamino-2-sulfoaniline, 1-aminonaphthalene-4-sulfonic acid, 1-aminonaphthalene-3-sulfonic acid, 1-aminonaphthalene-5-sulfonic acid, 1-aminonaphthalene-6-sulfonic acid, 1-aminonaphthalene-7-sulfonic acid, 1-aminonaphthalene-3,7-disulfonic acid, 1-aminonaphthalene-3,6,8-trisulfonic acid, 1-aminonaphthalene-4,6,8-trisulfonic acid, 2-naphthylamine-5-sulfonic acid or -6- or -8-sulfonic acid, 2-aminonaphthalene-3,6,8-trisulfonic acid, 2-aminonaphthalene-6,8-disulfonic acid, 2-aminonaphthalene-1,6-disulfonic acid, 2 aminonaphthalene-1-sulfonic acid, 2-aminonaphthalene-1,5-disulfonic acid, 2-aminonaphthalene-3,6-disulfonic acid, 2-aminonaphthalene-4,8-disulfonic acid, 4-(β-sulfatoethylsulfonyl)aniline, 3-(β-sulfatoethylsulfonyl)aniline, 2-sulfo-5-(β-sulfatoethylsulfonyl)aniline, 2-sulfo-4-(β-sulfatoethylsulfonyl)aniline, 2-methoxy-4-(β-sulfatoethylsulfonyl)aniline, 2-methoxy-5-methyl-4-(β-sulfatoethylsulfonyl)aniline, 2,5-dimethoxy-4-(β-sulfatoethylsulfonyl)aniline, 2-amino-5-(β-sulfatoethylsulfonyl)phenol, 2-amino-4-(β-sulfatoethylsulfonyl)phenol, 2-amino-6-(β-sulfatoethylsulfonyl)naphthalene-8-sulfonic acid, 2-amino-8-(β-sulfatoethylsulfonyl)naphthalene, 6-sulfonic acid, 2-amino-5-(β-

sulfatoethylsulfonyl)naphthalene-7-sulfonic acid and 2-amino-7-(β-sulfatoethylsulfonyl)naphthalene-5-sulfonic acid.

Aromatic amines of the diazo component Z-D-NH_2 with the fiber reactive residue Z originate, for example, from aromatic amines of the general formulas (6a) and (6b)



(6a)



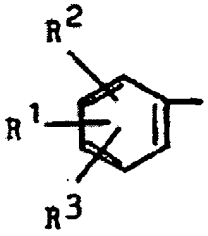
(6b)

in which M, p, R", R^2 and R^3 have the above given especially preferred meanings, where the benzene ring in formula (6a) and (6b) can additionally contain a hydroxy group in ortho position to the amino group $-NH_2$.

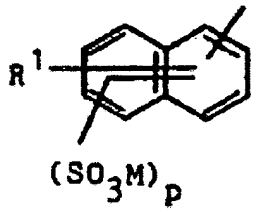
Amines of general formula (6) are, for example:

1,3-diaminobenzene, 1,3-diaminobenzene-4-sulfonic acid, 1,3-diaminobenzene-4,6-disulfonic acid, 1,4-diaminobenzene, 1,4-diaminobenzene-2-sulfonic acid, 1,4-diaminobenzene-2,5-disulfonic acid, 1,4-diamino-2-methylbenzene, 1,4-diamino-2-methoxybenzene, 1,3-diamino-4-methylbenzene, 1,5-diamino-4-methylbenzene-2-sulfonic acid, 1,5-diamino-4-methoxybenzene-2-sulfonic acid, 1,3-diaminobenzene-5-sulfonic acid, 1,3-diamino-5-methylbenzene, 2,6-diaminonaphthalene, 2,6-diaminonaphthalene-4,8-disulfonic acid, 2-amino-5-methylaminonaphthalene-1-sulfonic acid, 2-amino-5-methylaminonaphthalene-1,7-disulfonic acid and 1,4-diaminonaphthalene-6-sulfonic acid.

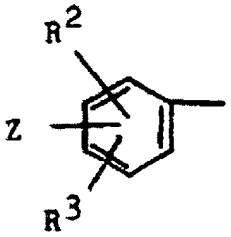
Preferred residues D in formulas (4a) and (4b) are ones of the general formulas (5c) and (5d) or (6c) and (6d)



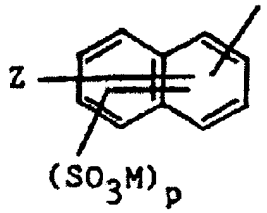
(5c)



(5d)

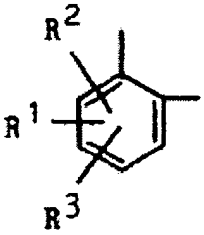


(6c)

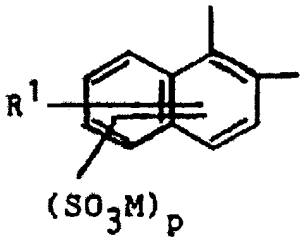


(6d)

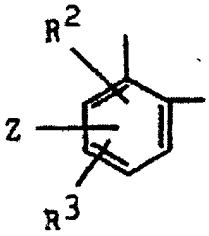
in which R^1, R^2, R^3, Z, M and p have the meanings given above, and preferred residues D in formula (4c) are ones of the general formulas (5e) and (5f) or (6e) and (6f)



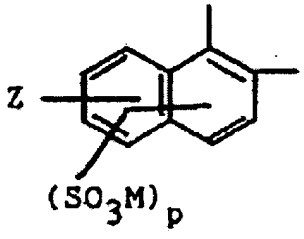
(5e)



(5f)



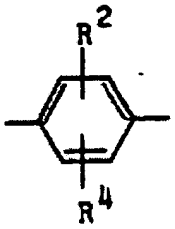
(6e)



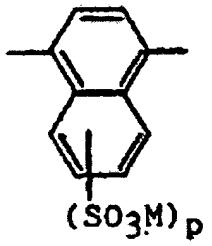
(6f)

in which R^1, R^2, R^3, Z, M and p have the meanings given above.

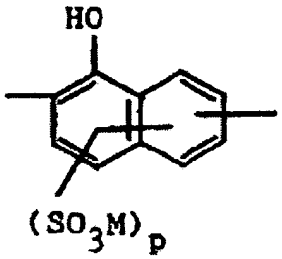
Aromatic residues E of a compound capable of coupling and diazotization and having the general formula H-E-NH_2 are, for example, ones of the general formulas (7a), (7b) and (7c)



(7a)



(7b)



(7c)

in which

R^2, M and p have the meanings given above and

R^4 is a hydrogen atom, an alkyl group with 1-4 C atoms such as the methyl or ethyl group, an alkoxy group with 1-4 C atoms such as the methoxy and ethoxy group, a chlorine atom, an alkanoylamino group with 2-5 C atoms such as the acetylamino and propionylamino groups, the benzoylamino group, ureido group, a phenylureido group, an alkylureido group with 1-4 C atoms in the alkyl residue, a phenylsulfonyl group or an alkylsulfonyl group with 1-4 C atoms.

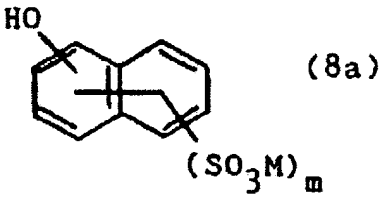
Compounds of formula H-E-NH_2 are, for example:

aniline, 3-methylaniline, 3-chloroaniline, 2,5-dimethylaniline, 2,5-dimethoxyaniline, 3-methoxyaniline, 3-methyl-6-methoxyaniline, 3-aminophenylurea, 3-acetylamino-6-methylaniline, 2-amino-4-acetylaminobenzene-1-sulfonic acid, 1-mainonaphthalene, 1-aminonaphthalene-6- or -7- or -8-sulfonic acid, 3-acetylaminoaniline, 2-methylaniline, 2-methoxyaniline, 3-benzoylaminoaniline, 2,3-dimethylaniline, 3,5-dimethylaniline, 1-amino-2-methoxy-5-acetylaminobenzene, 3-propionylaminoaniline, 3-butyrylaminoaniline, 2-sulfo-5-acetylaminoaniline, 2-amino-5-naphthol-7-sulfonic acid and 2-amino-8-naphthol-6-sulfonic acid.

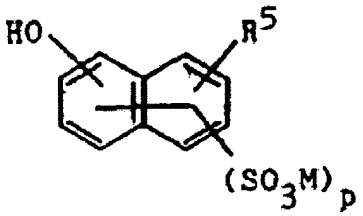
Residues K of the coupling component preferably derive [from] the aniline, naphthalene, pyrazole and acylacetarylide series; they can have fiber reactive groups.

Coupling components of the H-K of the aniline and naphthalene series are, for example, the anilines, N-mono- and N,N-disubstituted anilines, m-phenylenediamines and their derivatives, naphthenesulfonic acids, aminonaphthalenes, naphthols, hydroxynaphthoic acid derivatives, aminonaphthalenesulfonic acids or aminonaphtholsulfonic acids.

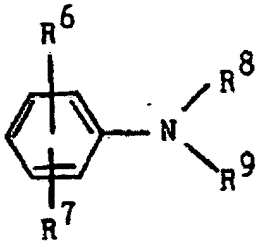
Coupling components of the formula H-K that do not carry any fiber reactive groups of the general formula (3) are, for example, compounds of the general formula (8a) through (8g)



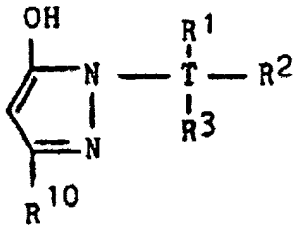
(8a)



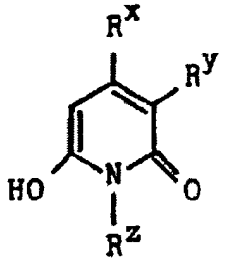
(8b)



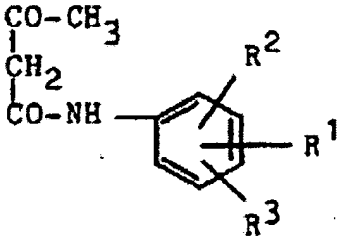
(8c)



(8d)

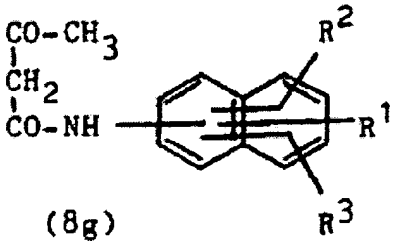


(8e)



(8f)

oder



(8g)

in which

R^1, R^2, R^3, p and M have the meanings given above,

m stands for the number zero, 1, 2 or 3 (where these groups mean a hydrogen atom if m is equal to zero),

R^5 means alkylureido with alkyl groups having 1-6 C atoms, phenylureido, phenylureido substituted in the phenyl residue by chlorine, methyl, methoxy, nitro, sulfo and/or carboxy and/or a group $-SO_2-Y$, with Y having the meaning given above, alkanoylamino with 2-7 C atoms such as acetylamino and propionylamino, cyclohexanoylamino, benzoylamino or benzoylamino substituted in the benzene residue by chlorine, methyl, methoxy, nitro, sulfo and/or carboxy and/or a group $-SO_2-Y$, with Y having the above meaning,

R^6 means hydrogen, alkyl with 1-4 C atoms like methyl and ethyl, alkoxy with 1-4 C atoms like methoxy and ethoxy, bromine, chlorine or alkanoylamino with 2-7 C atoms like acetylamino and propionylamino,

R^7 means hydrogen, alkyl with 1-4 C atoms like methyl and ethyl, alkoxy with 1-4 C atoms like methoxy and ethoxy, chlorine or alkanoylamino with 2-7 C atoms like acetylamino and propionylamino, ureido or phenylureido,

R^8 is hydrogen or alkyl with 1-4 C atoms, which can be substituted by hydroxy, cyano, carboxy, sulfo, sulfato, methoxycarbonyl, ethoxycarbonyl or acetoxy,

R^9 is alkyl with 1-4 C atoms, which can be substituted by hydroxy, cyano, carboxy, sulfo, sulfato, methoxycarbonyl, ethoxycarbonyl or acetoxy, or benzyl or phenyl or phenyl substituted by alkyl with 1-4 C atoms, alkoxy with 1-4 C atoms, chlorine and/or sulfo,

R^{10} is hydrogen, alkyl with 1-4 C atoms like methyl, cyano, carboxy, carbalkoxy with 2-5 C atoms like carbomethoxy and carbethoxy, carbamoyl or phenyl and preferably carbomethoxy or carbethoxy and especially methyl or carboxy,

T stands for a benzene or a naphthalene ring, preferably a benzene ring,

R^x is hydrogen or alkyl with 1-4 C atoms like methyl, or an alkyl with 1-4 C atoms substituted by alkoxy with 1-4 C atoms like methoxy or cyano, or is phenyl, preferably methyl,

R^y is hydrogen, sulfo or a sulfoalkyl with an alkyl residue with 1-4 C atoms like sulfomethyl, or cyano or carbamoyl, and

R^z is hydrogen, alkyl with 1-6 C atoms, preferably 1-4 C atoms, which can be substituted by phenyl or sulfophenyl or by hydroxy, amino, methoxy, ethoxy, carboxy, sulfo, acetylamino, benzoylamino or cyano, cyclohexyl, phenyl or phenyl substituted by carboxy, sulfo, benzoylamino, acetylamino, methyl, methoxy, cyano and/or chlorine and is preferably hydrogen or alkyl with 1-4 C atoms, which can be substituted by phenyl, sulfo or sulfophenyl.

Compounds of general formula (8) are, for example:

1-naphthol-3-sulfonic acid, 1-naphthol-4-sulfonic acid, 1-naphthol-5-sulfonic acid, 1-naphthol-8-sulfonic acid, 1-naphthol-3,6-disulfonic acid, 1-naphthol-3,8-disulfonic acid, 2-naphthol-5-sulfonic acid, 2-naphthol-6-sulfonic acid, 2-naphthol-7-sulfonic acid, 2-naphthol-8-sulfonic acid, 2-naphthol-3,6-disulfonic acid, 2-naphthol-6,8-disulfonic acid, 2-naphthol-3,6,8-trisulfonic acid, 1-acetylamino-8-hydroxynaphthalene-3,6-disulfonic acid, 1-benzoylamino-8-hydroxynaphthalene-3,6-disulfonic acid, 1-acetylamino-8-hydroxynaphthalene-4,6-disulfonic acid, 1-benzoylamino-8-hydroxynaphthalene-4,6-disulfonic acid, 2-acetylamino-5-hydroxynaphthalene-7-sulfonic acid, 3-acetylamino-5-hydroxynaphthalene-7-sulfonic acid, 2-methylamino-8-hydroxynaphthalene-6-sulfonic acid or 2-(3'- and 4'-sulfophenyl)-amino-8-hydroxynaphthalene-6-sulfonic acid, 3-(3'- and 4'-sulfophenyl)-amino-8-hydroxynaphthalene-6-sulfonic acid, N,N-di-(β-sulfoethyl)aniline and its derivatives that have been mono- or disubstituted in the benzene ring by methyl, methoxy and/or ethoxy, N-ethyl-N-(β-sulfoethyl)aniline, N-(β-carboxyethyl)aniline and derivatives mono- or disubstituted in the benzene ring by methyl, methoxy and/or ethoxy, furthermore 1-[3'-(β-

chloroethylsulfonyl)benzoylamino]-3,6-disulfo-8-naphthol, 1-[3'-(vinylsulfonyl)benzoylamino]-3,6-disulfo-8-naphthol, 1-[3'-(vinylsulfonyl)benzoylamino]-4,6-disulfo-8-naphthol, 1-[3'-(β-sulfatoethylsulfonyl)benzoylamino]-4,6-disulfo-8-naphthol, 2-[3'-(β-chloroethylsulfonylbenzoylamino]-6-sulfo-8-naphthol, 2-[3'-(vinylsulfonyl)benzoylamino]-6-sulfo-8-naphthol, 3-[3'-(β-chloroethylsulfonyl)benzoylamino]-6-sulfo-8-naphthol, 3-[3'-(vinylsulfonyl)benzoylamino]-6-sulfo-8-naphthol, 2-[N-methyl-N-(β-sulfatoethylsulfonyl)amino]-6-sulfo-8-naphthol, 3-[N-methyl-N-(β-sulfatoethylsulfonyl)-amino]-6-sulfo-8-naphthol, 2-[N-ethyl-N-(β-sulfatoethylsulfonyl)-amino]-6-sulfo-8-naphthol, 1-[N'-(3'-β-chloroethylsulfonylphenyl)ureido]-3,6-disulfo-8-naphthol, 1-[N'-(3'-vinylsulfonylphenyl)ureido]-3,6-disulfo-8-naphthol, 1-[N'-(3'-vinylsulfonylpropyl)ureido]-3,6-disulfo-8-naphthol, 1-[N'-(3'-β-chloroethylsulfonylphenyl)ureido]-4,6-disulfo-8-naphthol, 1-[N'-(3'-vinylsulfonylphenyl)ureido]-4,6-disulfo-8-naphthol, 1-[N'-(3'-β-chloroethylsulfonylphenyl)ureido]-4,6-disulfo-8-naphthol, 1-[N'-(3'-vinylsulfonylphenyl)ureido]-4,6-disulfo-8-naphthol, 1-[N'-(3'-β-chloroethylsulfonylpropyl)ureido]-4,6-disulfo-8-naphthol, 2-[N'-(3'-β-sulfatoethylsulfonylphenyl)ureido]-6-sulfo-8-naphthol, 2-[N'-(3'-β-chloroethylsulfonylpropyl)ureido]-6-sulfo-8-naphthol, 3-[N'-(3'-β-chloroethylsulfonylphenyl)ureido]-6-sulfo-8-naphthol and 3-[N'-(3'-vinylsulfonylpropyl)ureido]-6-sulfo-8-naphthol.

Of particular importance here are sulfo group-containing coupling components that optionally carry azo groups such as 1 or 2 azo groups, which couple in o or p position to a hydroxy and/or amino group, for example 2-acetylamino-5-hydroxynaphthalene-7-sulfonic acid, 2-acetylamino-8-hydroxynaphthalene-6-sulfonic acid, 1-acetylamino-8-hydroxynaphthalene-3,6-disulfonic acid, 1-benzoylamino-8-hydroxynaphthalene-3,6-disulfonic acid, 1-acetylamino-8-hydroxynaphthalene-4,6-disulfonic acid or 1-benzoylamino-8-hydroxynaphthalene-4,6-disulfonic acid.

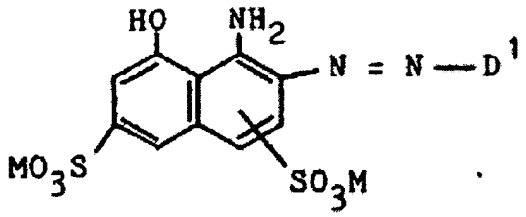
Pyrazolone coupling components are, for example, 3-methyl-, 3-carboxy- and 3-(C_2-C_5-alkoxycarbonyl)-5-pyrazolones which have in position 1 hydrogen, phenyl optionally substituted by methyl, ethyl, fluorine, chlorine, bromine, trifluoromethyl, methoxy, ethoxy, cyano, phenoxy, phenylsulfonyl, methylsulfonyl, sulfo, benzoyl, acetyl, acetylamino, nitro, hydroxy, carboxy, carbamoyl or sulfamoyl or sulfo-substituted 1- or 2-naphthyl, for example:

1-(2'-methoxy-5'-methylphenyl)-, 1-(2'-chloro-5'-sulfophenyl)-, 1-(2'-methoxy-5'-sulfophenyl)-, 1-(2'-methyl-4'-sulfophenyl)-, 1-(2',5'-dichloro-4'-sulfophenyl)-, 1-(2',5'-disulfophenyl)-, 1-(2'-carboxyphenyl)-, 1-(3'-sulfophenyl)-, 1-(4'-sulfophenyl)-, 1-(3'-sulfamoylphenyl)-3-carboxy-5-pyrazolone, 1-(3'- or 4'-sulfophenyl)-, 1-(2'-chloro-4'- or -5'-sulfphenyl)-, 1-(2'-methyl-4'-sulfophenyl)-, 1-(4',8'-disulfo-8-naphthyl)-, 1-(6'-sulfo-1-naphthyl)-3-methyl-5-pyrazolone, 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester, 5-pyrazolone-3-

carboxylic acid ethyl ester, 5-pyrazolone-3-carboxylic acid, 1-[4'-(β-sulfatoethylsulfonyl)-2'-sulfo]-phenyl-3-methylpyrazol-5-one, 1-[4'-(β-sulfatoethylsulfonyl)]-phenyl-3-carboxypyrazol-5-one and 1-(4'-sulfophenyl)-3-carboxypyrazol-5-one.

Pyridone coupling components are, for example, 1-ethyl-2-hydroxy-4-methyl-5-carbonamidopyridone-6,1-(2'-hydroxyethyl)-2-hydroxy-4-methyl-5-carbonamido-pyridone-6, (4'-sulfo-1-phenyl)-2-hydroxy-4-methyl-5-carbonamidopyridone-6, 1-(2'-sulfoethyl)-2-hydroxy-4-methyl-5-cyanopyridone-6, 1-ethyl-2-hydroxy-4-sulfomethyl-5-carbonamidopyridone-6, 1-ethyl-2-hydroxy-4-methyl-5-sulfomethylpyridone-6, 1-methyl-2-hydroxy-4-methyl-5-cyanopyridone-6, 1-methyl-2-hydroxy-5-acetylpyridone-6, 1,4-dimethyl-2-hydroxy-5-cyanpyridone-6, 1,4-dimethyl-2-hydroxy-5-carbonamidopyridone-6, 2,6-dihydroxy-4-ethyl-5-cyanopyridine, 2,6-dihydroxy-4-ethyl-5-carbonamidopyridine, 1-ethyl-2-hydroxy-4-methyl-5-sulfomethylpyridon-6, 1-methyl-2-hydroxy-4-methyl-5-methylsulfonylpyridone-6, 1-carboxymethyl-2-hydroxy-4-ethyl-5-phenylsulfonylpyridone-6 and 1-(2'-sulfoethyl)-2-hydroxy-4-carboxypyridone-6 and acetoacetylarylamide coupling components are, for example, acetoacetyl-(2-methoxy-4-sulfo-5-methyl)aniline, acetoacetyl-(2,4-dimethoxy-5-methyl)aniline and acetoacetyl-(4-β-sulfatoethylsulfonyl)aniline.

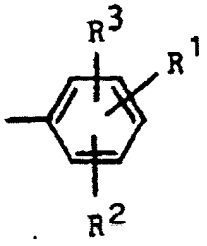
As coupling component H-K one may additionally mention in particular: 1-amino-8-hydroxynaphthalene-3,6- and 4,6-disulfonic acids as well as their arylazo coupling products obtainable by acid coupling and having the general formula (9a)



(9a)

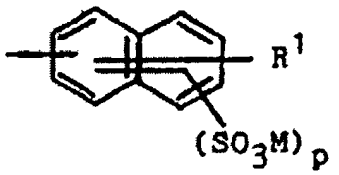
in which

D^1 can be a residue of a diazo component, for example a residue of the general formulas (10a) or (10b)



(10a)

or

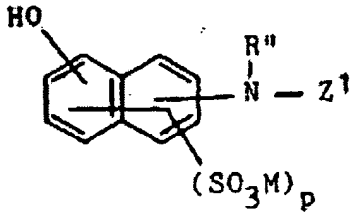


(10b)

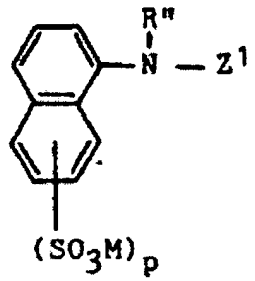
in which R^1, R^2, R^3, M and p have the meanings given above.

Individual residues D^1 are, for example: phenyl, 2-sulfophenyl, 3-sulfophenyl, 4-sulfophenyl, 2,4-disulfophenyl, 2,5-disulfophenyl, 3,5-disulfophenyl, 1,5-disulfonaphth-2-yl, 4,8-disulfonaphth-2-yl, 3,6,8-trisulfonaphth-2-yl, 4,6,8-trisulfonaphth-2-yl, 3,6,8-trisulfonaphth-1-yl, 4,6,8-trisulfonaphth-1-yl, 4-sulfonaphth-1-yl, 1-sulfonaphth-2-yl, 3-acetylaminophenyl, 4-acetylaminophenyl, 4-acetylamino-2-sulfophenyl, 5-acetylamino-2-sulfophenyl, 4-nitrophenyl, 4-nitro-2-sulfophenyl, 6-acetylamino-4,8-disulfonaphth-2-yl, 4-(β-sulfatoethylsulfonyl)phenyl and 3-(β-sulfatoethylsulfonyl)phenyl.

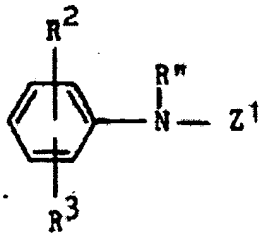
Coupling components that contain the fiber reactive groups of formula (3) in accordance with the invention or in which the fiber reactive groups can be inserted, optionally not until after the coupling reaction, are, for example, compounds of the general formulas (11a) through (11h) or their Z^1-free precursors:



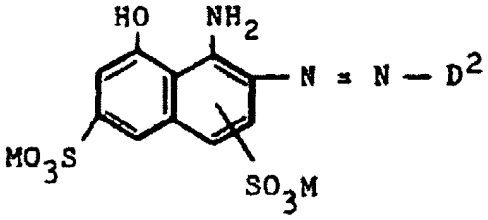
(11a)



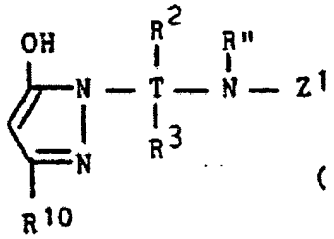
(11b)



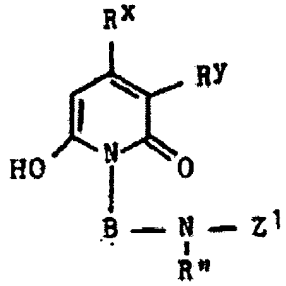
(11c)



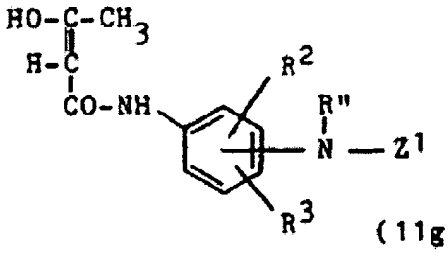
(11d)



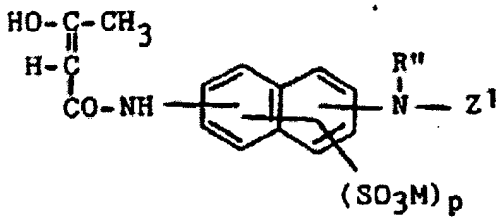
(11e)



(11f)



(11g)



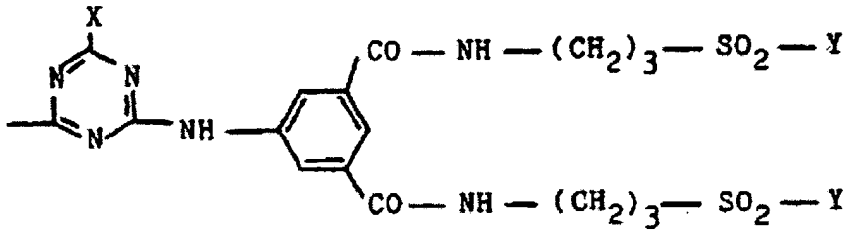
(11h)

in which

R", R^2, R^3, R^{10}, T, M, p, R^x, R^y and D^2 have the meanings especially the preferred meanings given above,

B is alkyl with 1-4 C atoms, benzyl or phenylethyl or phenyl or benzyl, phenylethyl or phenyl substituted in the benzene ring by fluorine, chlorine, bromine, methyl, methoxy, ethyl, ethoxy, cyano, sulfo, carboxy, acetyl, nitro, carbamoyl and/or sulfamoyl, where in the case of "benzyl" and "phenylethyl" the group –N(R")-Z^1 is bonded to the benzene ring.

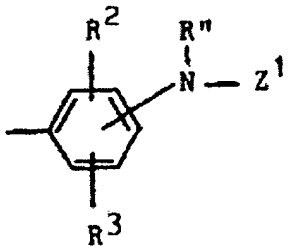
Z^1 is a residue of the general formula (3a)



(3a)

with X and Y having the meaning given above and

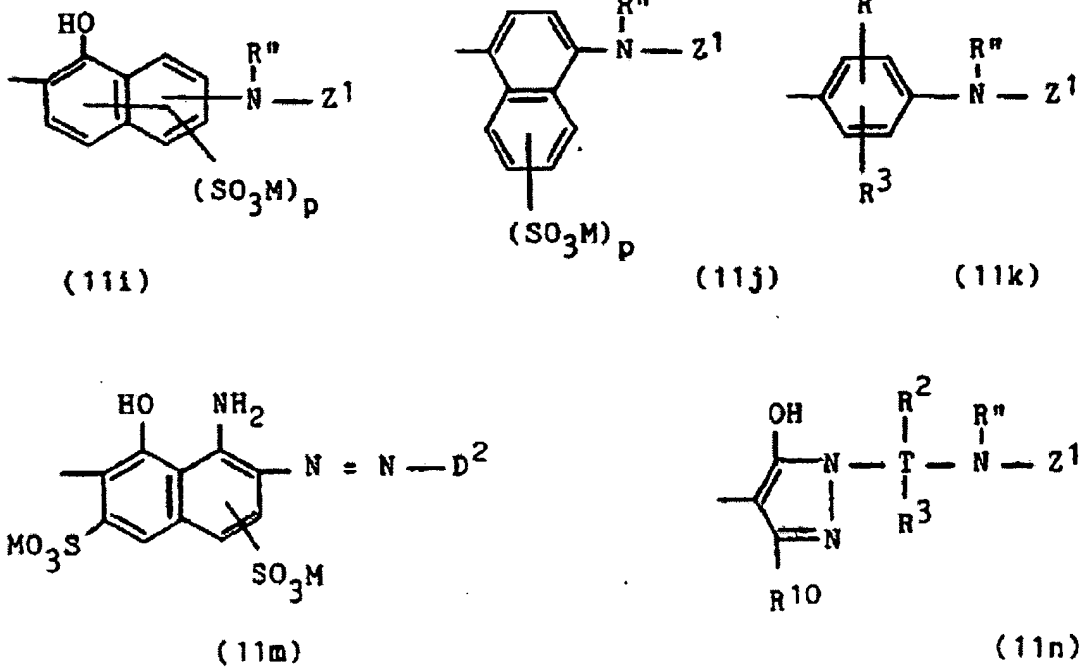
D^2 being a residue of a diazo component with the fiber reactive group of the general formula (3) and preferably a residue of the general formula (12)



(12)

with R", R^2, R^3 and Z^1 having the meaning given above.

The residues K in general formulas (4a) and (4b) are preferably the monovalent residues of compounds of the above general formulas (11a) through (11h), where the free bond leading to azo groups in formula (11a) is in ortho position to the hydroxy group, which is preferably bonded in alpha position to the naphthalene residue and in formula (11b) it is in para position to the group –N(R")-Z^1 and in formula (11c) it is in ortho position or preferably in para position to the group –N(R")-Z^1. Preferred here are the residues of the general formulas (11i), (11j), (11k), (11m) and (11n)

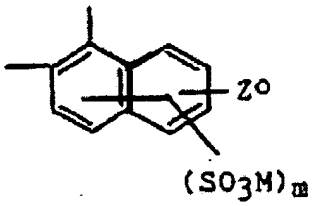


in which the individual terms of the formula have the above especially preferred meanings.

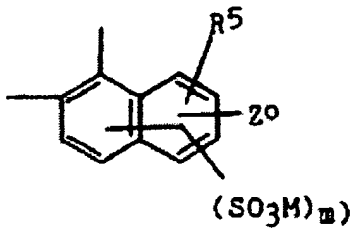
The said coupling components of general formulas (11a) and (11d) through (11h) can be prepared from their Z^1-free starting compounds, i.e., the amino starting compounds that have instead of the group –N(R")-Z^1 the group –N(R")-H, by reaction with a compound of the general formula X-Z^1 with X and Z^1 having the meanings given above. On the other hand, the compounds of general formulas (11b) and (11c) are not themselves useful as coupling components. They must be used as coupling components in the form of their Z^1-free amino compounds; after the coupling reaction the fiber reactive residue Z^1 can be introduced into the thus formed azo compound by reaction with a compound of the general formula X-Z^1. This method can also be chosen for the Z^1-free amino starting compounds of compounds (11a) and (11d) through (11h).

Provided the azo compounds in accordance with the invention contain the fiber reactive residue of general formula (3) in the diazo component, the residue K can have another known fiber reactive residue as the fiber reactive group. It can be introduced into the amino group containing starting coupling components either after the coupling reaction or before the coupling reaction by a reaction with the corresponding known fiber reactive acylation agent and by known methods.

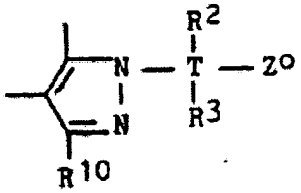
Residues K in general formula (4c), to which a metal complex binding oxygen atom is bound and that optionally contain the group Z are in particular ones of the formulas (13a) through (13f)



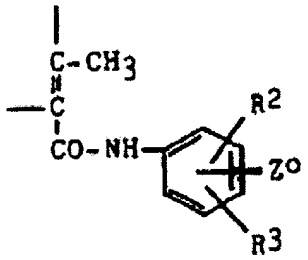
(13a)



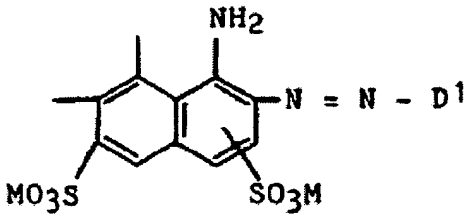
(13b)



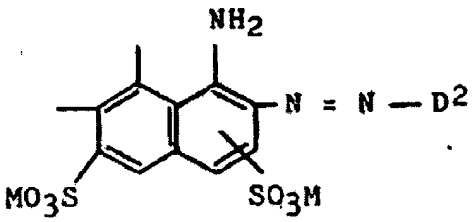
(13c)



(13d)



(13e)



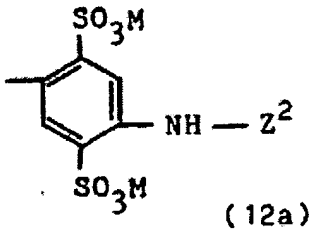
(13f)

in which Z° has one of the meanings of R^{1} or Z and the other formula members have one of the above meanings.

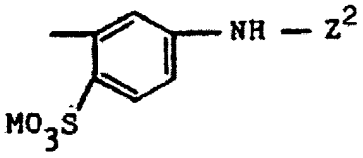
Aromatic diamines of the residue of formula (12) are, for example:

1,3-diaminobenzene, 1,3-diaminobenzene-4-sulfonic acid, 1,3-diaminobenzene-4,6-disulfonic acid, 1,4-diaminobenzene, 1,4-diaminobenzene-2-sulfonic acid, 1,4-diaminobenzene-2,5-disulfonic acid, 1,4-diamino-2-methylbenzene, 1,4-diamino-2-methoxybenzene, 1,3-diamino-4-methylbenzene, 1,4-diaminobenzene-2,6-disulfonic acid, 1,5-diamino-4-methylbenzene-2-sulfonic acid, 1,5-diamino-4-methoxybenzene-2-sulfonic acid, where in all of these diamino compounds a primary or secondary amino group has been substituted by the fiber reactive residue Z^1.

Preferred residues D^2 of formula (12) are, for example, the residues of formulas (12a), (12b) and (12c)



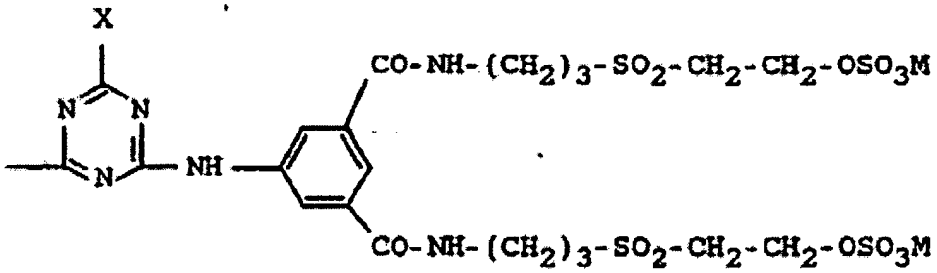
(12a)



(12b)

(12c)

in which Z^2 is a residue of the formula (3b)



(3b)

with X and M having the above meaning, where X is preferably a fluorine atom.

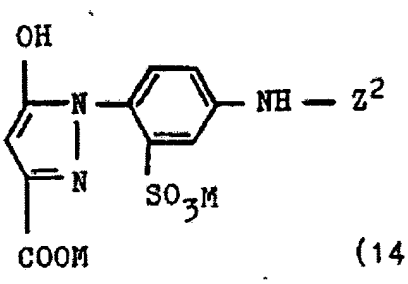
Fiber reactive diazo component residues D^2 are also ones that contain another fiber reactive group as group Z. Such residues D^2 are, for example, 4-(2-m-sulfophenylamino-4-

fluoro- or –chloro-s-triazine-6-yl)-amino-2-sulfohenyl, 4-(β-sulfatoethylsulfonyl)phenyl, 3-(β-sulfatoethylsulfonyl)phenyl and 4-vinylsulfonylphenyl.

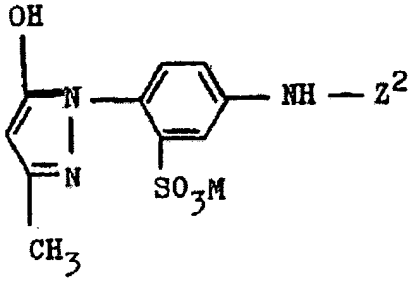
Coupling components that correspond to the compounds of general formulas (11a) through (11h) and that have a hydrogen atom instead of the residue Z^1, into whose free amino groups the residue Z^1 can be introduced, if necessary not until after the completion of coupling, are, for example:

1-(3'- or 4'-aminophenyl)-, 1-(2'-sulfo-5'-aminophenyl)- and 1-(2'-methoxy-5'-aminophenyl)-3-carboxy-5-pyrazolone, 1-(3'- or 4'-aminophenyl)-3-methyl-5-pyrazolone, 1-(6-amino-4',8'-disulfonaphthyl-2')-3-carboxy-5-pyrazolone.

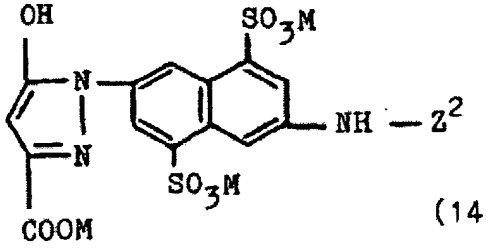
Preferred fiber reactive coupling components corresponding to formulas (13a) and (13b) are, for example, compounds of formulas (14a) through (14f):



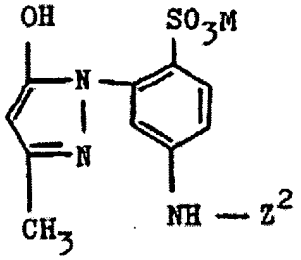
(14a)



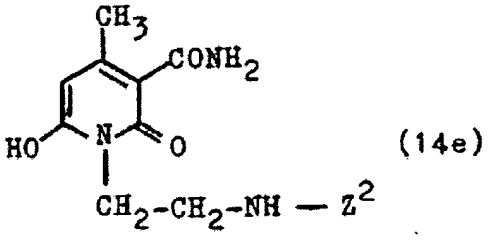
(14b)



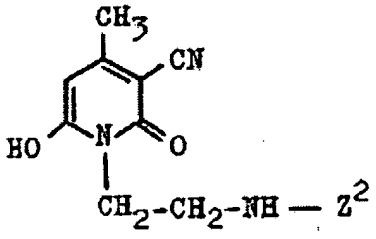
(14c)



(14d)



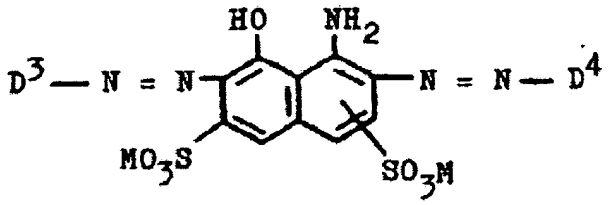
(14e)



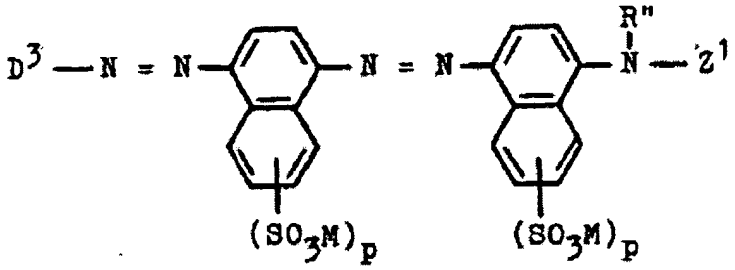
(14f)

in which M and Z^2 have the meanings given above.

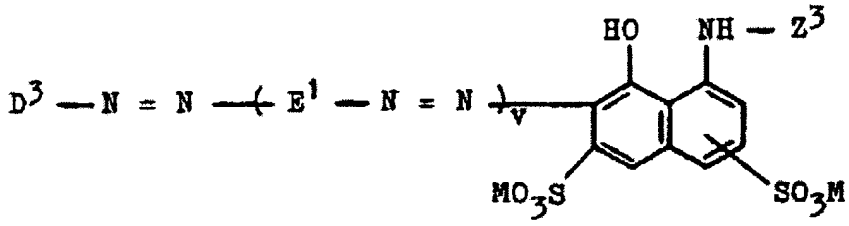
Of the azo dyes of general formula (1) in accordance with the invention the mono- and diazo compounds of the general formulas (15), (16a), (16b), (16c), (16d), (16e), (16f) and (17) can be emphasized in particular:



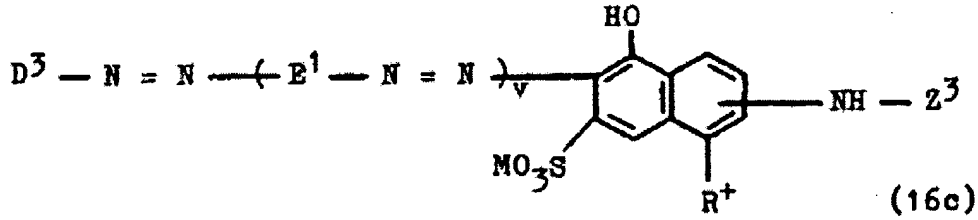
(15)



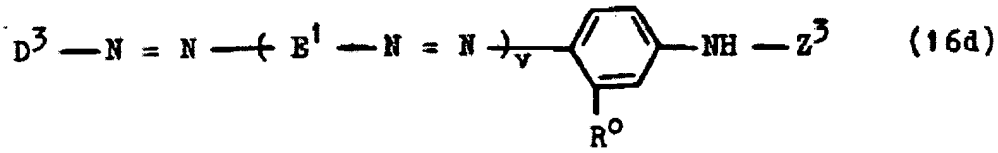
(16a)



(16b)



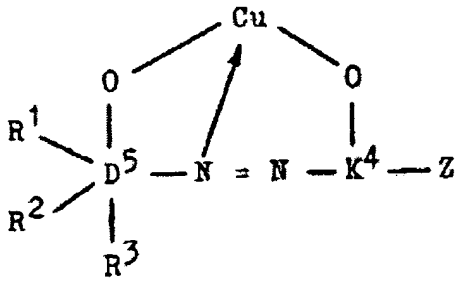
(16c)



(16d)

$$D^2 - N = N - K^2 \qquad (16e)$$

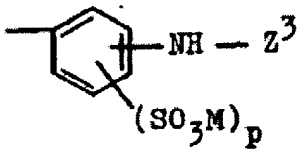
$$D^1 - N = N - K^3 \qquad (16f)$$



(17)

Here:

in formula (15) D^3 and D^4 have meanings that are the same or different from each other and each is a residue of a diazo component, of which at least one contains a fiber reactive group of the general formula (3) in which R" stands for a hydrogen atom, preferably a fiber reactive group Z^1 or Z^2, Z^1 has the meaning given above or is preferably a group Z^2 and M has the above meaning; preferably D^3 and D^4, which can be the same or different from each other, is each a residue D^1 or D^2 in correspondence with the above indicated and defined general formulas (10a) and (10b) or (12), especially preferably a mono- or disulfophenyl or mono-, di- or trisulfonaphthyl residue, or a residue of formula (12A)



(12A)

in which

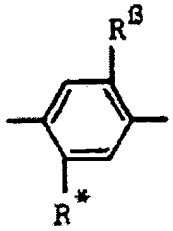
Z^3 is a residue of the above defined formula (3a) or preferably formula (3b) and

p and M have the meanings given above;

in formula (16a) D^3, p, R" and Z^1 have the meanings given above, where R" is preferably a hydrogen atom and D^3 is preferably a residue D^1 of formula (10a) or (10b), especially preferably a monosulfo- or disulfophenyl or a monosulfo-, disulfo- or trisulfonaphthyl residue;

in formulas (16b), (16c) and (16d) D^3, M and v have the meanings given above, where D^3 is preferably a residue D^1 of the formula (10a) or (10b), especially preferably a monosulfo- or disulfophenyl or a monosulfo-, disulfo- or trisulfonaphthyl residue,

E^1 is a residue of formulas (7A)



(7A)

in which R^β and R*, which can be the same or different from each other, each means a hydrogen atom, or the methyl, methoxy or ethoxy group,

R^o is the acetylamino or ureido group and

R* is a hydrogen atom or a sulfo group;

in formula (16e) D^2 is a residue of the above given and defined general formula (12), where in residue Z^1 the residue R" is preferably a hydrogen atom and Z^1 is especially preferably a residue of the general formula (3b), and K^2 means a residue of the above given and defined general formulas (8a), (8b), (8d) or (8e);

in formula (16f) D^1 means a residue of the general formula (10a) or (10b) and K^3 means a residue of the general formulas (14a) through (14f);

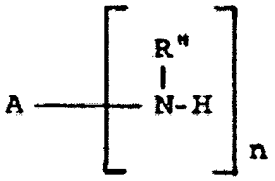
in formula (17) D^5 means a benzene or naphthalene nucleus, R^1, R^2 and R^3 have the above especially preferred meanings, where in the case that D^5 stands for a naphthalene nucleus, R^2 is a hydrogen atom and R^3 is a hydrogen atom or a sulfo group, the oxy group on D^5 and K^4 is in ortho position to the azo group, K^4 is a naphthalene nucleus, which can be substituted by 1 or 2 sulfo groups, and preferably is substituted, and Z is the said fiber reactive group of general formula (3a) or preferably a group of the formula $-NH-Z^2$ with Z^2 having the meaning of the general formula (3b).

The dyes in accordance with the invention can be produced in the usual manner of synthesis of dyes, for example by reacting the dye precursors that are known to the specialist for the corresponding class of dyes with the usual synthesis methods for this class of dyes, where at least one of these dye precursors contains a fiber reactive group of general formula (3). For instance, mono- and diazo dyes corresponding to general formula (1), for example, can be synthesized by reacting their diazo and coupling components in the procedure of diazotization and coupling that is conventional for this, where the diazo or coupling component or both (each) contain a fiber reactive group of general formula (3). In the case of the synthesis of diazo dyes the diazo or coupling component can already contain the second azo group. Diazo components that can be used in accordance with the invention are the usual aromatic carbocyclic and

heterocyclic amino compounds for fiber reactive azo dyes that can contain the fiber reactive groups of the general formula (3) and that contain the usual coupling components for synthesis of fiber reactive azo dyes, for example those of the naphthol, aniline, naphthylamine, aminonaphthol, pyrazolone and pyridine series, where optionally the coupling component contains the fiber reactive group of general formula (3). Such diazo and coupling components are, for example, the many compounds described above, which correspond to the general formulas (5), (6), (7), (8), (9), (10), (11) and (14) or derived from them.

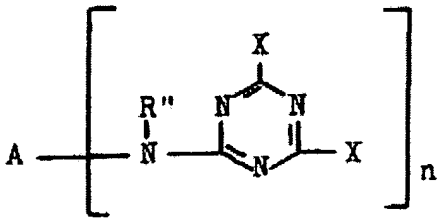
The diazotization and coupling reactions take place in the usual way so that the diazotization as a rule takes place at a temperature between -5°C and +15°C and a pH value under 2 by means of a start acid and alkali nitrite in preferably an aqueous medium and the coupling reaction as a rule takes place at a pH value between 1.5 and 4.5 in the case of the amino group containing coupling component and a pH value between 3 and 7.5 in the case of the hydroxy group containing coupling component and at a temperature between 0 and 25°C, also preferably in an aqueous medium.

The new dyes of general formula (1) can also be produced in accordance with the invention so that a cyanuric halide like cyanuric fluoride or cyanuric chloride is reacted with an amino compound of the general formula (18)



(18)

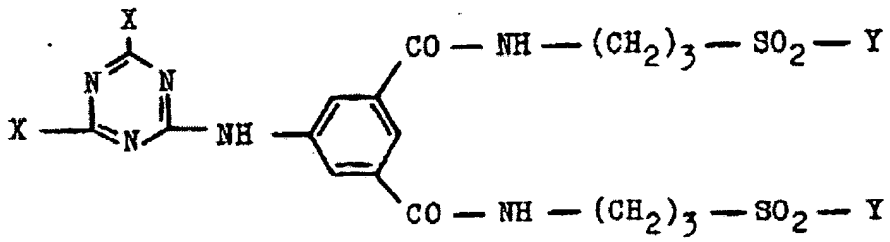
in which A, R" and n have the meanings given above, and an amino compound of the general formula (19) H_2N-Z* (19), with Z* having the meaning given above, in any order. For instance, one can initially react an amino compound of general formula (18) with the cyanuric halide to form a dihalotriazinylamino compound of the general formula (20)



(20)

with A, X, R" and n having the meaning given above, and then converting this product to the end dye (1) by a reaction with an amino compound of general formula (19) in an equivalent

amount, or one can first react an amino compound of general formula (19) with the cyanuric halide to form a dihalotriazinylamino compound of the general formula (21)



(21)

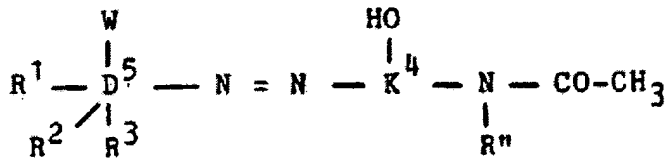
with R", X and Y having the meaning given above and reacting this with an equivalent amount of the compound of general formula (18) to form end dye (1). The condensation reactions between the cyanuric halide or the dihalotriazinylamino compounds (20) and (21) and the amino compounds (18) and/or (19) can take place in the usual way of the reaction of a cyanuric halide or a dihalotriazinylamino compound with amino compounds, thus in an organic or preferably aqueous medium, especially preferably in an aqueous medium with the addition of acid-binding agents, like

alkali or alkaline earth carbonates, alkali or alkaline earth hydrogen carbonates or hydroxides or alkali acetates, where the alkali and alkaline earth metals are preferably sodium, potassium or calcium. Acid binding agents are also tertiary amines such as pyridine, triethylamine or quinoline. If these condensation reactions take place in organic or aqueous organic media, the (proportional) organic solvent is acetone, dioxane or dimethylformamide.

The condensation reactions between cyanuric fluoride and the amino compounds as a rule take place at a temperature between -10°C and +10°C, preferably between -5°C and +5°C, and at a pH value between 1.0 and 7.0, preferably between 4 and 5. The reaction of the difluorotriazinylamino compounds of general formulas (20) or (21) with an amino compound of general formula (18) or (19) takes place, for example, at a temperature between 0 and 50°C, preferably between 10 and 30°C, and at a pH value between 2 and 8, preferably between 5 and 7, and care should be taken that the fiber reactive group is not damaged in the weakly alkaline region. The condensation reactions with the cyanuric halide take place under the same conditions, but at temperatures 10-20°C higher.

In the synthesis according to the invention of heavy metal complex azo dyes, for example ones corresponding to general formulas (4c) and (17), as a rule one starts with heavy metal-free azo compounds that contain, bound in the coupling component, a phenolic or naphtholic hydroxy group in ortho position or vicinal position to the azo group and whose diazo component residue contains a hydrogen atom or a hydroxy group or a lower alkoxy group like methoxy bound in

ortho position to the azo group and that additionally contain a bound acylamino residue, such as an acylamino residue corresponding to the general formula –N(R")-acyl, in which acyl stands for the acyl residue of an organic acid, such as a lower alkanoic acid, and R" has the meaning given above, for example one starts with the starting compound corresponding to the general formula (22)



(22)

in which R^1, R^2, R^3, D^5, K^4 and R" have the meanings given above and W is a hydrogen atom or a hydroxy or methoxy group bonded to D^5 in ortho position to the azo group, and this acylamino group containing starting azo compound is reacted with a heavy metal-affording agent like a heavy metal salt by analogy with known and conventional procedures or it is, in the case of the formation of a copper complex azo dye, also subjected to an oxidative or dealkylating copperization reaction, which is carried out in the usual way. The resulting heavy metal complex azo compounds with the acylamino group can then be converted to the dyes of general formula (1) in accordance with the invention by analogy with the known procedures involving saponification (hydrolysis) of the acylamino group to an amino group with cyanuric fluoride and the fiber reactive amino compound in correspondence with general formula (19).

The dyes that have β-sulfatoethylsulfonyl or β-phosphatoethylsulfonyl groups as the groups $-SO_2$-Y can in accordance with the invention also be produced by reacting a dye that contains the group of the above general formula (1) with the above meaning, in which however one or more of the formula residues Y is a β-hydroxyethyl group, with a sulfatization agent or phosphatization agent like concentrated sulfuric acid and sulfuric acid containing sulfur trioxide or an aqueous concentrated phosphoric acid and polyphosphoric acid by analogy with known procedures, where the sulfatization as a rule takes place at a temperature between 10 and 25°C and the phosphatization at a temperature between 20 and 100°C.

The starting dyes with the β-hydroxyethylsulfonyl groups can be synthesized by analogy with the above data for preparation of the dyes in accordance with the invention, by using either the corresponding dye precursors that contain these β-hydroxyethylsulfonyl groups or reacting an amino dye of general formula (18) and an amino compound of general formula (19), but in which Y stands for the β-hydroxyethyl group, with a cyanuric halide in accordance with the above reaction conditions.

Dyes corresponding to the above general formula (1) in accordance with the invention, in which one or more of the formula residues Y is a vinyl group, can also be obtained in accordance with the invention from dyes corresponding to general formula (1), in which at least one of the formula residues Y is a β-sulfatoethyl or β-haloethyl group, by converting the β-sulfatoethyl or β-haloethyl group to a vinyl group by treatment with an aqueous alkali, for example sodium hydrogen carbonate or sodium hydroxide, in an aqueous medium at a temperature of 0-60°C and a pH value of 9-11.

The starting compounds of general formula (19) have not yet been described up to now. They can be produced by reacting γ-(β'-hydroxyethylsulfonyl)propylamine in a twofold molar amount with 5-nitrobenzene-1,3-di(carboxylic acid chloride) in an aqueous medium at a pH between 7 and 9.5 and a temperature of 20-60°C and reducing the resulting nitrobenzene compound to an aniline compound (19) with Y equal to the β-hydroxyethyl group, by the usual procedure of reducing an aromatic nitro compound to an amino group, for example by catalytic reduction by means of hydrogen on a metal catalyst like Raney nickel in an aqueous medium, for example.

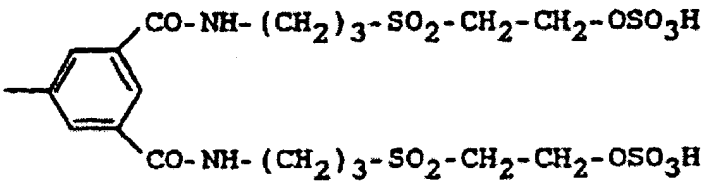
The compounds of general formula (19) in which Y stands for the β-hydroxyethyl groups can in a substantially known procedure be converted to the fiber reactive compounds with Y equal to the corresponding fiber reactive groups of one of the meanings given above, for example to their ester derivatives with Y equal to the sulfato, phosphate or acetyloxy group by a reaction with, for example, 100% sulfuric acid or sulfuric acid containing sulfur trioxide or with concentrated phosphoric acid or polyphosphoric acid or by means of glacial acetic acid.

The compounds of general formula (1) in accordance with the invention are suitable as fiber reactive dyes for dyeing and printing hydroxy group containing fibers, especially cotton, and also for synthetic or natural polyamide fibers like wool. The known dyeing and printing methods for fiber reactive dyes, especially ones for fiber reactive dyes that have a combination of the fiber reactive groups of the fluorotriazine and vinylsulfone series are suitable as dyeing methods. The dyes in accordance with the invention can be used with particular advantage at 20-40°C and the cold padding process. Application is possible in a wide temperature range, and the dyes are characterized by high depth of color and high degree of fixation.

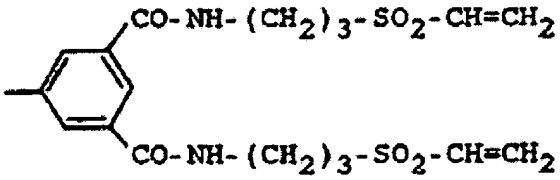
The following examples serve to illustrate the invention. Parts are parts by weight and the percentage data are percent by weight, unless otherwise noted. Parts by weight refer to parts by volume as kilograms to liters. The compounds described by formulas in the examples are given in the form of the free acids; in general they are prepared and isolated in the form of their alkali metal salts such as the lithium, sodium or potassium salts and used in the form of their salts for dyeing. Likewise, the starting compounds and components indicated in the form of their free

salts in the following examples, especially the table examples, can be used in the synthesis as such or in the form of their salts, preferably alkali metal salts.

The formula residue Z^x, which occurs in the formulas in the following examples, means the 3,5-di{carboxylic acid-[γ-(β'-sulfatoethylsulfonyl)propylamide]}phenyl group corresponding to general formula (25) given in the form of the free acid below and residue Z^v means the 3,5-di[carboxylic acid (γ-vinylsulfonyl)propylamide]phenyl residue corresponding to formula (26):



(25)

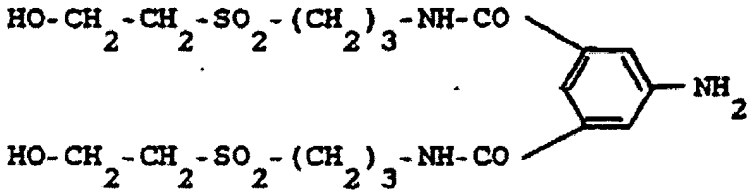


(26).

The absorption maxima (λ_{max}) in the visible region that are given for the compounds in accordance with the invention were measured by means of their alkali metal salts in an aqueous solution. In the table examples the λ_{max} values are given in parentheses for the color shade data; wavelength data refer to nm.

Example A

The starting compound of formula (19A)



(19A)

is prepared as follows:

About 365 parts hydrogen chloride is introduced into 750 parts 3-aminopropane-1-ol up to formation of the hydrochloride. 1190 parts thionyl chloride is slowly added to the still liquid

hydrochloride at 70-85°C. The now barely stirrable reaction mixture is stirred for one more hour and then dissolved in 600 parts water. The solution is slowly added to a solution of 780 parts thionyl glycol and 400 parts sodium hydroxide in 1500 parts water while maintaining a pH from 11 to 11.5 by means of sodium hydroxide and a temperature of a maximum of 60°C. The mixture is stirred a little longer at about 50°C and then the water is distilled out at reduced pressure, the residue is digested in 1500 parts by volume methanol, the undissolved material is filtered out and the γ-(β'-hydroxyethylthio)propylamine is isolated from the residue after removing the solvent, by fractional distillation at 132-140°C/3 mbar.

270 parts of this compound is dissolved in 243 parts 30% hydrochloric acid. 2 parts sodium tungstate is added and then 395 parts 35% aqueous hydrogen peroxide is slowly added, keeping the highly exothermic reaction under 98°C.

After cooling the resulting batch of the hydrochloride of γ-(β'-hydroxyethylsulfony)propylamine is mixed with 200 parts water. A pH of 9 is established with sodium hydroxide and a solution of 236 parts 5-nitrobenzene-1,3-di(carboxylic acid chloride) with 240 parts by volume acetone is added while maintaining a pH value of 7-9 by means of sodium hydroxide and a temperature of about 30°C. After the end of the reaction the batch is cooled to 0-5°C and the 5-nitrobenzene-1,3-di-{carboxylic-[γ-(β'-hydroxyethylsulfony)propylamide]} is isolated by filtration; it has a melting point of 101-104°C.

The resulting nitrobenzenedicarboxylic acid amide compound is suspended in 1200 parts water and catalytically reduced to the amine compound of formula (19A) using water and Raney nickel at 25-60°C and an excess hydrogen pressure of about 40 bar. After the end of the reduction the catalyst is filtered out. Compound (19A) crystallizes upon cooling the filtrate to 0-5°C. It has a melting point of 145-147°C and is uniform according to thin layer chromatography.

Example B

The 5-aminobenzene-1,3-bis[γ-(β'-hydroxyethylsulfonyl)-N-propylcarboxylic amide] prepared under Example A can be converted to its fiber reactive derivatives, for example the bissulfato, bisphosphato or bisacetyloxy compound, in the usual way, for example by reaction in 100% sulfuric acid or phosphoric acid or in glacial acetic acid.

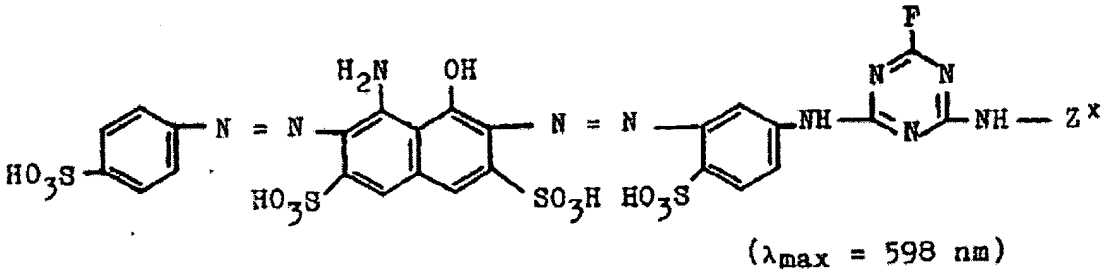
Both the β-hydroxyethylsulfonyl compound and the β-sulfato-, β-phosphato- and β-acetyloxyethylsulfonyl compounds of this 5-nitrobenzene-1,3-dicarboxylic acid amide serve as diazo component for the synthesis of the dyes in accordance with the invention. If the β-hydroxyethylsulfonyl compound in accordance with formula (19A) is used as diazo component in the synthesis of the dyes in accordance with the invention, the β-hydroxyethylsulfonyl groups can be converted, by analogy with known procedures, either to intermediate compounds during

the synthesis of the azo dye or to the corresponding β-sulfato, β-phosphato or β-acetyloxy derivatives in the ready-to-use azo dye itself.

Example 1

31.6 parts of a suspension of 1-amino-8-naphthol-3,6-disulfonic acid in 300 parts water is added to 17.3 parts of a hydrochloric acid diazotized aniline-4-sulfonic acid at 5°C. Coupling is carried out for 8 h at a pH value between 1 and 2 and then a solution of the diazonium salt of 92.2 parts of the secondary condensation product of 1,3-phenylenediamine-4-sulfonic acid, cyanuric fluoride and 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbony]aniline is added. The pH is adjusted to 5-6 with sodium carbonate and the coupling reaction is carried out in this pH range and at a temperature of about 20°C. Then the resulting synthesis solution is evaporated under reduced pressure at 60°C.

A black electrolyte-containing powder of the alkali metal salt of the compound of the formula

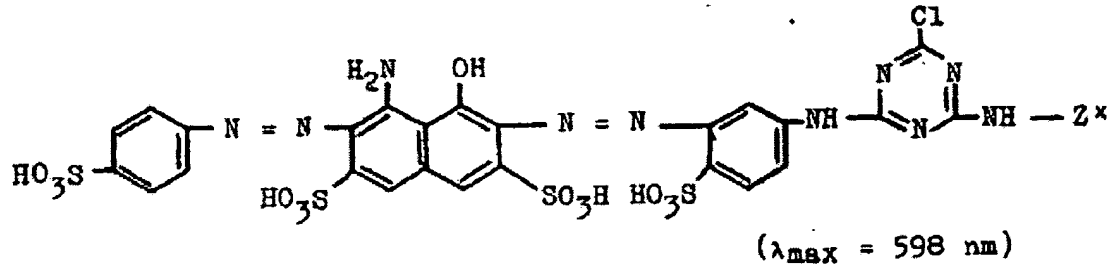


is obtained, where Z^x has the above meaning, in which dyes cotton, for example, fast marine blue shades. One should note in particular the washing and perspiration fastness.

Example 2

To produce a diazo compound in accordance with the invention one proceeds by analogy with Example 1 using a monoazo compound from aniline-4-sulfonic acid as diazo compound and 1-amino-8-naphthol-3,6-disulfonic acid as coupling component and the solution of the diazonium salt from 93.9 parts of the secondary condensation product from 1,3-phenylenediamine-4-sulfonic acid, cyanuric chloride and 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbony]aniline is then added to the hydrochloric acid solution of this monoazo compound. The coupling reaction is then carried out at a pH between 5 and 6, as in Example 1.

The dye in accordance with the invention is obtained as the sodium salt; it has, written in the form of the free acid, the formula



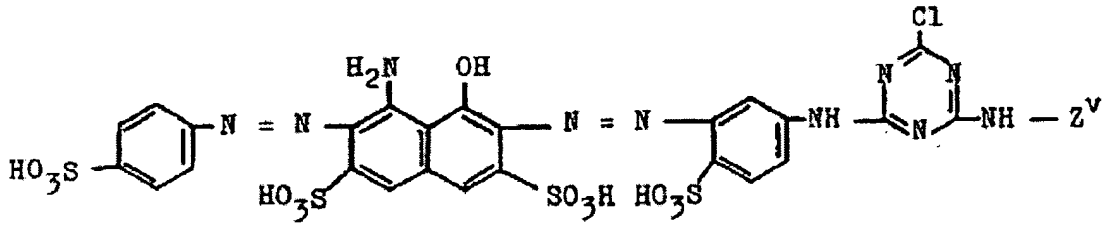
(λ_{max} = 598 nm)

with Z^x having the above meaning, and it exhibits very good dye properties. When used for the usual application and fixing processes for fiber reactive dyes it produces marine blue dyeings and prints with good fastness properties on the materials indicated in the description, especially cellulose fiber materials like cotton.

Example 3

To convert the dye of Example 2 in accordance with the invention to its vinylsulfonyl form it is dissolved in water at 15-20°C and the solution is adjusted to a pH of 10.5 with sodium hydroxide. The pH value falls to about 9 after a short time, which points to the elimination of the sulfato groups. When the pH value no longer decreases, the elimination of the sulfato groups is complete; this takes about 15 min. Then the solution is adjusted to a pH of 5 with hydrochloric acid and the dye is precipitated out by adding potassium chloride.

The dye in accordance with the invention has, in the form of the free acid, the formula

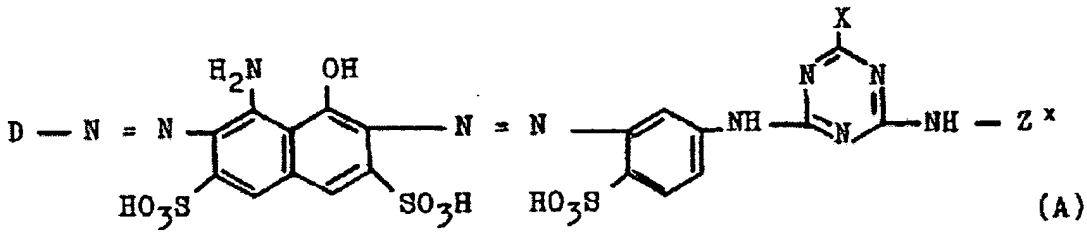


(λ_{max} = 598 nm)

with Z^v having the meaning given above; the dye in accordance with the invention has very good dye properties and with the usual application and fixing methods for fiber reactive dyes, for example for dyeing loose fiber materials, colors these materials a soft marine blue shade with good fastness properties, which correspond to those of the dye of Example 2.

Examples 4-16

Other dyes in accordance with the invention corresponding to a general formula (A)



(A)

in which Z^x is the residue of the earlier given formula (25) and X is equal to fluorine or chlorine, are described in the following table examples with the help of the components given there. They can be prepared in a manner in accordance with the invention, for example by analogy with Embodiment Example 1, using the diazo component D-NH_2 coupled to 1-amino-8-naphthol-3,6-disulfonic acid as divalent coupling component acid coupled, 1,3-phenylenediamine-4-sulfonic acid, cyanuric fluoride or cyanuric chloride and the amine H_2N-Z^x corresponding to general formula (19). These new compounds corresponding to general formula (1) likewise have very good fiber reactive dye properties and dye cellulose fiber materials in particular, the strong fast shades indicated in the table.

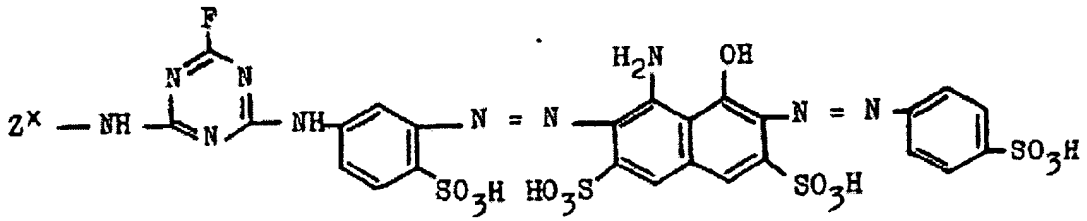
Example	Residue D	Residue X	Shade
4	2-Chloro-4-sulfophenyl	Fluorine	Greenish marine blue (615)
5	ditto	Chlorine	Greenish marine blue (615)
6	2-Chloro-4,6-disulfophenyl	Fluorine	Greenish marine blue (618)
7	ditto	Chlorine	Marine blue
8	4-Chloro-2-sulfophenyl]	Fluorine	Marine blue
9	ditto	Chlorine	Marine blue
10	1,5-Disulfonaphth-2-yl	Fluorine	Greenish marine blue (610)
11	ditto	Chlorine	Greenish marine blue (612)
12	4-(β-Sulfatoethylsulfonyl)phenyl	Fluorine	Marine blue (604)
13	ditto	Chlorine	Marine blue
14	4-(β-Sulfatoethylsulfonyl)-2-sulfophenyl	Fluorine	Greenish marine blue (624)
15	5-(β-Sulfatoethylsulfonyl)-2-sulfophenyl	Chlorine	Greenish marine blue (615)
16	ditto	Fluorine	Greenish marine blue (615)

Example 17

18.8 parts 1,3-phenylenediamine-4-sulfonic acid is reacted with 14 parts cyanuric fluoride under vigorous agitation at 0°C. By adding an aqueous sodium carbonate solution the pH is kept between 4 and 5. Then 64 parts 3,5-bis-[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline is condensed at 20°C and a pH between 5 and 6. The resulting secondary condensation product is then diazotized with sodium nitrite at a temperature between 0 and 5°C in the usual way after the addition of hydrochloric acid. The

resulting diazonium salt solution is added to a suspension of 30.8 parts 1-amino-8-naphthol-3,6-disulfonic aid in 300 parts water. The coupling reaction takes place at a pH of 1.5-2.

The resulting monoazo compound is now mixed with a hydrochloric acid, aqueous solution of the diazonium compound containing 17.3 parts aniline-4-sulfonic acid; the coupling reaction to diazo dye is carried out at a pH between 4.5 and 5.5 and a temperature between 0-20°C. The compound in accordance with the invention is isolated by evaporating the solution, for instance by spray drying. One obtains a black electrolyte-containing powder containing the alkali metal salt in the compound of the formula

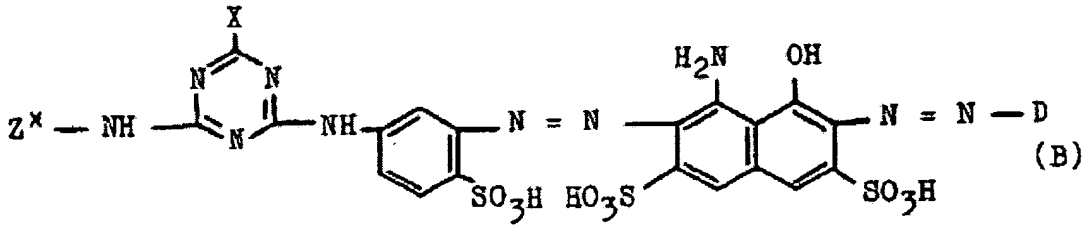


(λ_{max} = 609 nm)

with Z^x having the meaning given above, which by the usual dyeing and printing process is used for fiber reactive dyes on cotton produces reddish marine blue shades with good fastness is obtained. The lightfastness and washfastness are to be emphasized particularly.

Examples 18-23

Other dyes in accordance with the invention that correspond to a general formula (B)



(B)

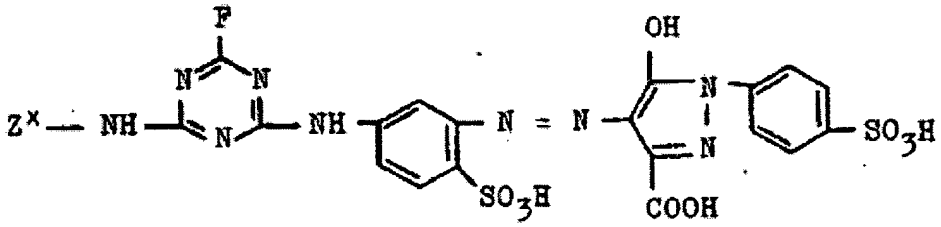
are described in the following table examples by means of the components listed there. They can be prepared in the manner in accordance with the invention, for example by analogy with Embodiment Example 17, using the neutrally coupled diazo component D-NH_2, 1-amino-8-naphthol-3,6-disulfonic acid as divalent coupling component and the condensation product from 1,3-phenylenediamine-4-sulfonic acid, cyanuric fluoride or cyanuric chloride and the amine of the formula N_2N-Z^x with Z^x having the meanings given above, as acid coupled diazo component.

These new compounds corresponding to general formula (1) likewise have very good fiber reactive dye properties and dye in particular cellulose fiber materials the strong fast shades indicated for each example.

Example	Residue D	Residue X	Shade
18	1,5-Disulfo-2-naphthyl	Fluorine	Marine blue (610)
19	2-Chloro-4,6-disulfophenyl	Fluorine	Marine blue
20	2-Chloro-4-sulfophenyl	Fluorine	Marine blue (616)
21	2-Methoxy-5-methyl-4-sulfophenyl	Fluorine	Marine blue
22	4-(β-Sulfatoethylsulfonyl)phenyl	Chlorine	Marine blue (612)
23	3,6,8-Trisulfo-2-naphthyl	Chlorine	Marine blue

Example 24

The condensation part of 18.8 parts 1,3-phenylenediamine-4-sulfonic acid, 18.5 parts cyanuric fluoride and 64 parts 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline is diazotized using hydrochloric acid, mixed with 28.5 parts 1-(4'-sulfophenyl)-3-carboxypyrazol-5-one and coupled at a pH between 5 and 7. The compound in accordance with the invention is precipitated from a neutral solution with potassium chloride and dried. The resulting alkali salt of the compound of the formula

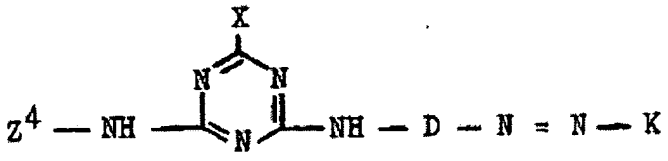


(λ_{max} = 408 nm)

with Z^x having the above meaning, dyes, for example cotton in fast color shades, by the usual dyeing processes for fiber reactive dyes. The lightfastness and perspiration fastness should be mentioned in particular.

Examples 25-55

Other dyes in accordance with the invention corresponding to a general formula (C)



(C)

described in the following table examples with the help of the components listed there. They can be prepared in a manner in accordance with the invention, for example by analogy with Embodiment Example 24, using the condensation product of a diaminobenzenesulfonic acid in correspondence with the formula H_2N-D-NH_2, cyanuric fluoride or cyanuric chloride and the amine of the general formula Z^4-NH_2, with Z^4 equal to the residue Z^x or Z^v having the above meaning as well as the coupling component H-K. These new compounds in correspondence with general formula (1) likewise have very good fiber reactive dye properties and dye cellulose fiber materials in particular the strong fast shades indicated for the relevant example.

① Bsp.	② Kupplungskomponente H-K	③ Diaminobenzolsulfonsäure	④ Z^4 ist ...	⑤ Rest X	⑥ Farbton
⑦ 25	1-Phenyl-3-carboxy-5-pyrazolon	⑰ 1,3-Diaminobenzol-4,6-disulfonsäure	Z^x	⑳ Fluor	㉒ gelb (407)
⑧ 26	1,4-Dimethyl-2-hydroxy-3-sulfo-6-pyridon	dito	Z^x	㉑ Chlor	㉓ grünstichig gelb
⑨ 27	1-Ethyl-4-methyl-3-carbamoyl-2-hydroxy-6-pyridon	⑱ dito	Z^x	Chlor	grünstichig gelb
28	dito	dito	Z^v	Chlor	grünstichig gelb
⑩ 29	1-(2'-Methyl-4'-sulfophenyl)-3-carboxy-5-pyrazolon	1,3-Diaminobenzol-4-⑲ sulfonsäure	Z^x	Fluor	gelb ㉔
⑪ 30	3,6-Disulfo-1-naphthol	dito	Z^x	Fluor	orange
⑫ 31	3,8-Disulfo-1-naphthol	dito	Z^x	Fluor	scharlach ㉕
⑬ 32	4,8-Disulfo-1-naphthol	dito	Z^x	Fluor	gelbstichig rot ㉖
⑭ 33	3-Sulfo-7-(3'-sulfophenyl)-amino-1-naphthol	dito	Z^x	Chlor	orange
⑮ 34	1-Ethyl-2-hydroxy-4-methyl-5-carbamoyl-6-pyridon	dito	Z^x	Fluor	gelb
⑯ 35	3-Sulfo-7-acetylamino-1-naphthol	dito	Z^x	Chlor	orange

Key:
1 Example
2 Coupling component H-K
3 Diaminobenzenesulfonic acid
4 Z^4 is ...
5 Residue X
6 Shade
7 1-Phenyl-3-carboxy-5-pyrazolone
8 1,4-Dimethyl-2-hydroxy-3-sulfo-6-pyridone

9 1-Ethyl-4-methyl-3-carbamoyl-2-hydroxy-6-pyridone
10 1-(2'-Methyl-4'-sulfophenyl)-3-carboxy-5-pyrazolone
11 3,6-Disulfo-1-naphthol
12 3,8-Disulfo-1-naphthol
13 4,8-Disulfo-1-naphthol
14 3-Sulfo-7-(3'-sulfophenyl)-amino-1-naphthol
15 1-Ethyl-2-hydroxy-4-methyl-5-carbamoyl-6-pyridone
16 3-Sulfo-7-acetylamino-1-naphthol
17 1,3-Diaminobenzene-4,6-disulfonic acid
18 ditto
19 1,3-Diaminobenzene-4-sulfonic acid
20 Fluorine
21 Chlorine
22 Yellow (407)
23 Greenish yellow
24 Yellow
25 Scarlet
26 Yellowish red

① Bsp.	② Kupplungskomponente H-K	③ Diaminobenzolsulfonsäure	④ Z^4 ist ...	⑤ Rest X	⑥ Farbton
⑦ 36	1-Naphthol-6-acetyl-amino-3-sulfonsäure	dito	Z^H	Fluor ⑯	orange
⑧ 37	1-(2'-Sulfoethyl)-4-methyl-3-cyano-2-hydroxy-6-pyridon	1,3-Diaminobenzol-4-sulfonsäure ⑭	Z^H	Chlor ⑰	gelb ⑱
38	⑨ dito	1,4-Diaminobenzol-2-sulfonsäure ⑮	Z^H	Fluor	gelb
⑩ 39	1-Ethyl-4-methyl-3-sulfomethyl-6-hydroxy-2-pyridon	1,3-Diaminobenzol-4-sulfonsäure ⑭	Z^H	Chlor	gelb
⑪ 40	1-(4'-Sulfophenyl)-3-carboxy-5-pyrazolon	dito	Z^H	Fluor	gelb (407) ⑲
⑫ 41	1-(4'-Sulfophenyl)-3-methyl-5-pyrazolon	dito	Z^H	Fluor	gelb (392) ⑳
42	dito	1,4-Diaminobenzol-2-sulfonsäure ⑮	Z^H	Fluor	gelb
43	1-Acetylamino-3,6-disulfo-8-naphthol ⑬	dito	Z^H	Fluor	rot
44	dito	dito	Z^V	Chlor	rot ㉑
45	dito	dito	Z^H	Chlor	rot

Key: 1 Example
2 Coupling component H-K
3 Diaminobenzenesulfonic acid
4 Z^4 is ...
5 Residue X
6 Shade
7 1-Naphthol-6-acetylamino-3-sulfonic acid
8 1-(2'-Sulfoethyl)-4-methyl-3-cyano-2-hydroxy-6-pyridone
9 ditto

10 1-Ethyl-4-methyl-3-sulfomethyl-6-hydroxy-2-pyridone
11 1-(4'-Sulfophenyl)-3-carboxy-5-pyrazolone
12 1-(4'-Sulfophenyl)-3-methyl-5-pyrazolone
13 1-Acetylamino-3,6-disulfo-8-naphthol
14 1,3-Diaminobenzene-4-sulfonic acid
15 1,4-Diaminobenzene-2-sulfonic acid
16 Fluorine
17 Chlorine
18 Yellow
19 Yellow (407)
20 Yellow (392)
21 Red

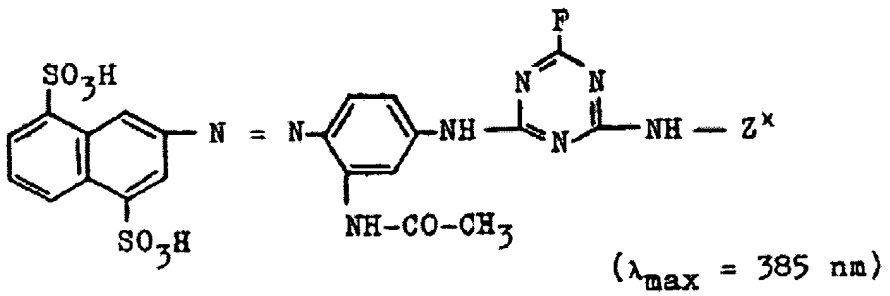
① Bsp.	② Kupplungskomponente H-K	③ Diaminobenzolsulfonsäure	④ Z^4 ist ...	⑤ Rest X	⑥ Farbton
46	⑦ dito	1,3-Diaminobenzol-4-sulfonsäure ⑮	Z^4	⑱ Chlor	⑳ rot (520)
⑧ 47	1-Benzoylamino-3,6-disulfo-8-naphthol	dito	Z^4	Chlor	㉑ rot (534)
⑨ 48	1-Benzoylamino-4,6-disulfo-8-naphthol	dito	Z^4	⑲ Fluor	rot (534)
⑩ 49	4,8-Disulfo-1-naphthol	1,3-Diaminobenzol-4-sulfonsäure ⑮	Z^4	Fluor	rot
⑪ 50	4-Sulfo-naphthol	dito	Z^4	Fluor	rot
⑫ 51	1-Benzoylamino-3,6-disulfo-8-naphthol	1,4-Diaminobenzol-2-sulfonsäure ⑯	Z^4	Chlor	rot
⑬ 52	1-Benzoylamino-4,6-disulfo-8-naphthol	dito	Z^4	Chlor	㉒ rot (512)
53	dito	1,3-Diamino-2-methyl-benzol-5-sulfonsäure ⑰	Z^4	Fluor	rot
54	dito	dito	Z^4	Chlor	rot
⑭ 55	3-Sulfo-7-(4'-sulfophenyl)-amino-1-naphthol	1,3-Diaminobenzol-4-sulfonsäure ⑮	Z^4	Fluor	rot

Key:
1 Example
2 Coupling component H-K
3 Diaminobenzenesulfonic acid
4 Z^4 is ...
5 Residue X
6 Shade
7 Ditto
8 1-Benzoylamino-3,6-disulfo-8-naphthol
9 1-Benzoylamino-4,6-disulfo-8-naphthol
10 4,8-Disulfo-1-naphthol
11 4-Sulfonaphthol
12 1-Benzoylamino-3,6-disulfo-8-naphthol
13 1-Benzoylamino-4,6-disulfo-8-naphthol
14 3-Sulfo-7-(4'-sulfophenyl)amino-1-naphthol

15	1,3-Diaminobenzene-4-sulfonic acid
16	1,4-Diaminobenzene-2-sulfonic acid
17	1,3-Diamino-2-methylbenzene-5-sulfonic acid
18	Chlorine
19	Fluorine
20	Red (520)
21	Red (534)
22	Red (512)

Example 56

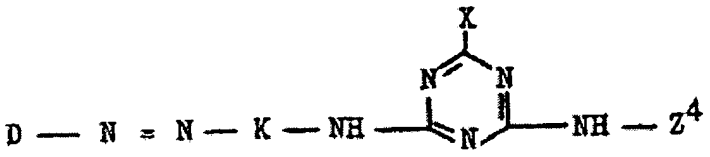
A solution of 30.3 parts 2-aminonaphthalene-4,8-disulfonic acid in 200 parts water is diazotized using hydrochloric acid at 0°C with 6.9 parts sodium nitrite and coupled with 15 parts 3-acetylaminoaniline at a pH between 4 and 5. The resulting azo compound is acylated with 19 parts cyanuric fluoride at a temperature of 0°C and a pH of 4 under vigorous agitation, the monocondensation product is reacted with 70 parts 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline at a pH of 5-6 and a temperature of 0-20°C and the resulting dye in accordance with the invention is precipitated with potassium chloride and isolated. The alkali metal salt of the formula



with Z^x having the above meaning, dyes cotton fast reddish yellow shades by the conventional dyeing methods for fiber reactive dyes. Of the types of fastness in particular the lightfastness, alkaline perspiration fastness and chlorine waterfastness should be noted.

Examples 57-70

Other dyes in accordance with the invention in correspondence with the general formula (D)



(D)

in which Z^4 is the residue Z^x or Z^v with the above meaning, D is the residue of the diazo component without fiber reactive group and K is the residue of an amino group containing coupling component in correspondence with the formula H-N-NH_2, are described in the following table examples with the help of the components listed there. They can be prepared in a manner in accordance with the invention, for example by analogy with Embodiment Example 56, using the diazo component D-NH_2, the coupling component H-K-NH_2, cyanuric chloride or cyanuric fluoride and the amine of the general formula H_2N-Z^4. The new compounds likewise have very good fiber reactive dye properties and dye cellulose fiber materials in particular the strong fast shades indicated for the relevant table example.

① Bsp.	② Rest D	③ Verbindung H-K-NH_2	④ Z^4 ist ...	⑤ Rest X	⑥ Farbton
⑦57	1,5-Disulfo-2-naphthyl	3-Acetylamino-anilin ⑬	Z^x	⑲ Fluor	gelb ㉑
⑧58	1,6-Disulfo-2-naphthyl	3-Amino-phenylharnstoff ⑭	Z^x	Fluor	goldgelb ㉒
59	⑨dito	N-(3-Aminophenyl)-N'-methyl-harnstoff ⑮	Z^x	Fluor	goldgelb
⑩ 60	6,8-Disulfo-2-naphthyl	3-Acetylamino-anilin ⑯	Z^x	Chlor ⑳	goldgelb
61	dito	2-Sulfo-5-acetylamino-anilin ⑰	Z^x	Fluor	goldgelb
⑪62	3,6,8-Trisulfo-2-naphthyl	3-Amino-phenylharnstoff ⑭	Z^x	Fluor	goldgelb (416)
63	dito	dito	Z^x	Chlor	goldgelb (408)
64	dito	dito	Z^x	Chlor	goldgelb
65	dito	N-Phenyl-N'-(3-amino-phenyl)-harnstoff ⑱	Z^v	Chlor	goldgelb
66	dito	N-(3-Aminophenyl)-N'-methyl-harnstoff ⑮	Z^v	Chlor	goldgelb
⑫67	4-(β-Sulfatoethyl-sulfonyl)-phenyl	3-Acetylamino-anilin ⑯	Z^v	Chlor	goldgelb

Key:
1 Example
2 Residue D
3 Compound H-K-NH_2
4 Z^4 is ...
5 Residue X
6 Shade
7 1,5-Disulfo-2-naphthyl

8	1,6-Disulfo-2-naphthyl
9	ditto
10	6,8-Disulfo-2-naphthyl
11	3,6,8-Trisulfo-2-naphthyl
12	4-(β-Sulfatoethylsulfonyl)phenyl
13	3-Acetylaminoaniline
14	3-Aminophenylurea
15	N-(3-Aminophenyl)-N'-methylurea
16	3-Acetylaminoaniline
17	2-Sulfo-5-acetylaminoaniline
18	N-Phenyl-N'-(3-aminophenyl)urea
19	Fluorine
20	Chlorine
21	Yellow
22	Golden yellow
23	Golden yellow (416)
24	Golden yellow (408)

① Bsp.	② Rest D	③ Verbindung H-K-NH_2	④ Z^4 ist ...	⑤ Rest X	⑥ Farbton
68	3-(β-Sulfatoethylsulfonyl)-phenyl ⑦	dito ⑩	Z^X	⑪ Fluor	goldgelb
69	6-(β-Sulfatoethylsulfonyl)-8-sulfo-2-naphthyl ⑧	dito	Z^X	Fluor	goldgelb ⑬
70	8-(β-Sulfatoethylsulfonyl)-6-sulfo-2-naphthyl ⑨	dito	Z^X	⑫ Chlor	goldgelb

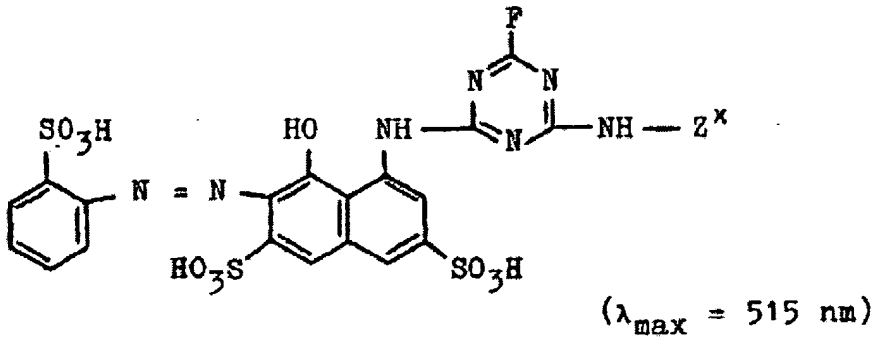
Key:

1	Example
2	Residue D
3	Compound H-K-NH_2
4	Z^4 is ...
5	Residue X
6	Shade
7	3-(β-Sulfatoethylsulfonyl)phenyl)
8	6-(β-Sulfatoethylsulfonyl)-8-sulfo-2-naphthyl
9	8-(β-Sulfatoethylsulfonyl)-6-sulfo-2-naphthyl
10	ditto
11	Fluorine
12	Chlorine
13	Golden yellow

Example 71

95 parts cyanuric fluoride are converted in the usual way first with 160 parts 1-amino-3,6-disulfo-8-naphthol and then with 325 parts 3,5-bis[γ-(β'-

sulfatoethylsulfonyl)propylaminocarbonyl]aniline to the dicondensation product, which is then added to a solution of the diazonium salt of 87 parts 1-aminobenzene-2-sulfonic acid; the coupling reaction takes place at a pH between 4 and 4.5. The dye in accordance with the invention that is formed is precipitated with potassium chloride. The alkali metal salt of the compound of the formula

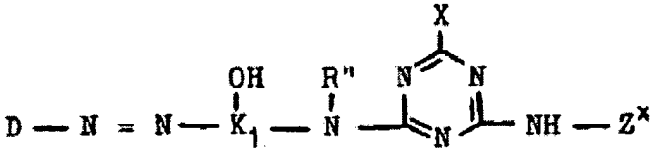


(λ_{max} = 515 nm)

with Z^x having the above meaning is obtained; it dyes cotton bright red fast shades. Of the types of fastness one can note in particular the washfastness and lightfastness of dyeings wetted with water or with a perspiration solution.

Examples 72-111

Other dyes in accordance with the invention corresponding to a general formula (E)



(E)

are described in the following table examples with the aid of the formula residues of formula (E). They can be prepared in a manner in accordance with the invention, for example by analogy with Embodiment Example 71, using the diazo component D-NH_2, the aminonaphtholsulfonic acid corresponding to a formula H(OH)K_1-NHR" as naphthol coupling component and cyanuric fluoride or cyanuric chloride and the amine of the formula H_2N-Z^x with Z^x being the residue of the previously given formula (25). These new compounds in correspondence with general formula (1) likewise have very good fiber reactive dye properties and dye cellulose fiber materials in particular the strong true shades given in the table.

① Bsp.	② Rest D	③ Kupplungs-komponente $H(OH)K_1$-NHR"	④ Rest X	⑤ Farbton
⑥ 72	4-Sulfo-1-naphthyl	⑲ 1-Amino-3,6-disulfo-8-naphthol	㉒ Fluor	㉔ rot
⑦ 73	6-Sulfo-1-naphthyl	dito	Fluor	rot
⑧ 74	1-Sulfo-2-naphthyl	dito	㉓ Chlor	rot
⑨ 75	5-Sulfo-2-naphthyl	dito	Fluor	rot
⑩ 76	6-Sulfo-2-naphthyl	dito	Chlor	rot
⑪ 77	4-Methoxy-2-sulfo-phenyl	dito	Chlor	㉕ blaustichig rot
⑫ 78	4-Phenoxy-2-sulfo phenyl	dito	Chlor	dito
12a 79	4-Methyl-2-sulfo-phenyl	dito	Fluor	rot
⑬ 80	4-Sulfo-phenyl	dito	Fluor	rot (519) ㉖
⑭ 81	3-Sulfo-phenyl	dito	Chlor	rot
⑮ 82	1,5-Disulfo-2-naphthyl	dito	Fluor	rot (520) ㉗
⑯ 83	4,8-Disulfo-2-naphthyl	dito	Chlor	rot
⑰ 84	2-Sulfo-phenyl	⑳ 1-Amino-4,6-disulfo-8-naphthol	Chlor	rot
85	⑱ dito	㉑ 1-Amino-4-sulfo-8-naphthol	Fluor	rotorange ㉘

Key:
1 Example
2 Residue D
3 Coupling component $H(OH)K_1$-NHR"
4 Residue X
5 Shade
6 4-Sulfo-1-naphthyl
7 6-Sulfo-1-naphthyl
8 1-Sulfo-2-naphthyl
9 5-Sulfo-2-naphthyl
10 6-Sulfo-2-naphthyl
11 4-Methoxy-2-sulfophenyl
12 4-Phenoxy-2-sulfophenyl
13 4-Sulfophenyl
14 3-Sulfophenyl
15 1,5-Disulfo-2-naphthyl
16 4,8-Disulfo-2-naphthyl
17 2-Sulfophenyl
18 ditto
19 1-Amino-3,6-disulfo-8-naphthol
20 1-Amino-4,6-disulfo-8-naphthol
21 1-Amino-4-sulfo-8-naphthol
22 Fluorine
23 Chlorine

24 Red
25 Bluish red
26 Red (519)
27 Red (520)
28 Red orange
29 4-Methyl-2-sulfophenyl

① Bsp.	② Rest D	③ Kupplungs-komponente H(OH)K_1-NHR"	④ Rest X	⑤ Farbton
⑥ 86	4,6-Disulfo-phenyl	⑰ 2-Amino-6-sulfo-8-naphthol	Fluor ㉔	rotorange ㉖
⑦ 87	4-Sulfo-phenyl	⑱ 2-Amino-7-sulfo-5-naphthol	Chlor ㉕	orange
⑧ 88	1,5-Disulfo-2-naphthyl	⑲ 2-Amino-7-sulfo-5-naphthol	Chlor	orange
89	⑨ dito	⑳ 2-Methylamino-7-sulfo-5-naphthol	Fluor	orange
90	dito	dito	Fluor	orange
⑩ 91	4-Methoxy-2-sulfo-phenyl	㉑ 3-Amino-7-sulfo-5-naphthol	Chlor	scharlach ㉗
⑪ 92	6,8-Disulfo-2-naphthyl	dito	Chlor	scharlach
⑫ 93	4-Methoxy-3-sulfo-phenyl	⑱ 2-Amino-7-sulfo-5-naphthol	Chlor	scharlach (499)
94	dito	㉑ 3-Amino-7-sulfo-5-naphthol	Fluor	scharlach
95	⑬ 4-(β-Sulfatoethyl-sulfonyl)-anilin	㉒ 1-Amino-3,6-disulfo-8-naphthol	Fluor	scharlach (490)
96	⑭ 3-(β-Sulfatoethyl-sulfonyl)-anilin	dito	Fluor	rot ㉘
97	⑮ 2-Sulfo-5-(β-sulfato-ethylsulfonyl)-anilin	dito	Chlor	rot
98	⑯ 4-(β-Sulfatoethyl-sulfonyl)-anilin	㉓ 1-Amino-4,6-disulfo-8-naphthol	Fluor	rot

Key:
1 Example
2 Residue D
3 Coupling component H(OH)K_1-NHR"
4 Residue X
5 Shade
6 4,6-Disulfophenyl
7 4-Sulfophenyl
8 1,5-Disulfo-2-naphthyl
9 ditto
10 4-Methoxy-2-sulfophenyl
11 6,8-Disulfo-2-naphthyl
12 4-Methoxy-3-sulfophenyl
13 4-(β-Sulfatoethylsulfonyl)aniline
14 3-(β-Sulfatoethylsulfonyl)aniline
15 2-Sulfo-5-(β-sulfatoethylsulfonyl)aniline
16 4-(β-Sulfatoethylsulfonyl)aniline
17 2-Amino-6-sulfo-8-naphthol

18 2-Amino-7-sulfo-5-naphthol
19 2-Amino-7-sulfo-5-naphthol
20 2-Methylamino-7-sulfo-5-naphthol
21 3-Amino-7-sulfo-5-naphthol
22 1-Amino-3,6-disulfo-8-naphthol
23 1-Amino-4,6-disulfo-8-naphthol
24 Fluorine
25 Chlorine
26 Red orange
27 Scarlet
28 Scarlet (499)
29 Scarlet (490)
30 Red

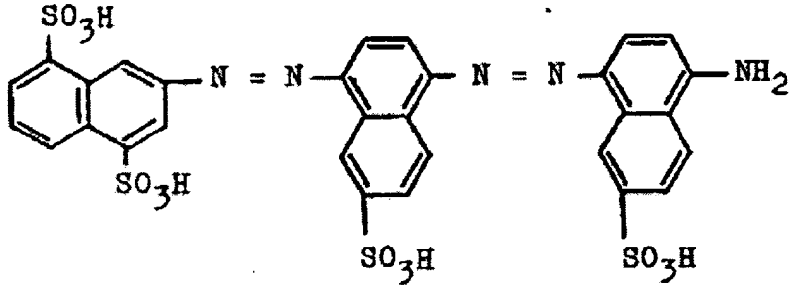
(1) Bsp.	(2) Rest D	(3) Kupplungs-komponente H(OH)K_1-NHR"	(4) Rest X	(5) Farbton
99	(6) dito	(17) 3-Amino-7-sulfo-5-naphthol	(22) Fluor	rotorange (24)
100	(7) 6-Sulfo-8-(β-sulfatoethylsulfonyl)-2-naphthyl	(18) 2-Amino-7-sulfo-5-naphthol	Fluor	rotorange
101	(8) 4-Carboxy-phenyl	(19) 1-Amino-3,6-disulfo-8-naphthol	Fluor	rot (498) (25)
102	(9) 2,4-Disulfo-phenyl	dito	Fluor	rotorange
103	(10) 2,5-Disulfo-phenyl	dito	Chlor (23)	rotorange
104	(11) 2-Sulfo-phenyl	(18) 2-Amino-7-sulfo-5-naphthol	Fluor	rotorange
105	(12) 3,6,8-Trisulfo-2-naphthyl	dito	Fluor	rotorange
106	dito	dito	Chlor	rotorange
107	(13) 4-(β-Sulfatoethyl-sulfonyl)-phenyl	(20) 1-(β-Aminoethyl)-4-methyl-3-carbamoyl-2-hydroxy-pyrid-6-on	Chlor	gelb (26)
108	dito	(21) 1-(β-Aminoethyl)-4-methyl-3-cyano-2-hydroxy-pyrid-6-on	Fluor	gelb
109	(14) 1-Sulfo-6-carboxy-2-naphthyl	(19) 1-Amino-3,6-disulfo-8-naphthol	Fluor	(27) blaustichig rot (545)
110	(15) 2-Sulfo-phenyl	(18) 2-Amino-7-sulfo-5-naphthol	Chlor	rotorange
111	(16) 1,5-Disulfo-2-naphthyl	dito	Fluor	(28) scharlach

Key:
1 Example
2 Residue D
3 Coupling component H(OH)K_1-NHR"
4 Residue X
5 Shade
6 ditto
7 6-Sulfo-8-(β-sulfatoethylsulfonyl)-2-naphthyl
8 4-Carboxyphenyl
9 2,4-Disulfophenyl

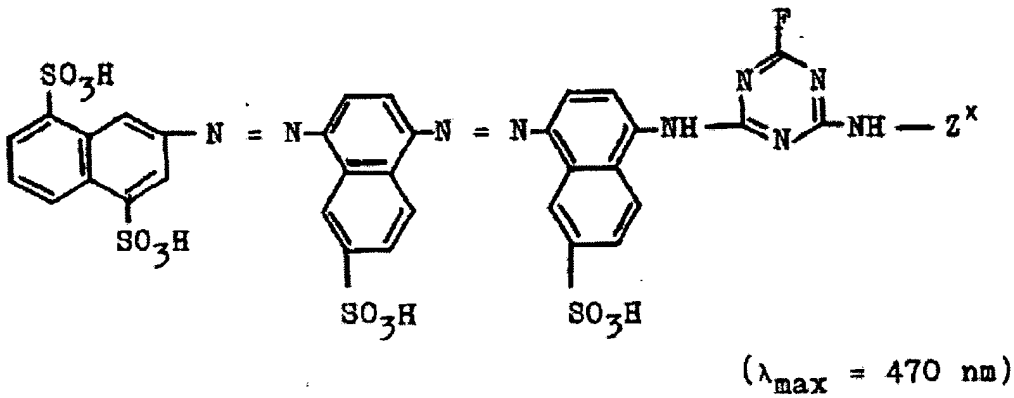
10	2,5-Disulfophenyl
11	2-Sulfophenyl
12	3,6,8-Trisulfo-2-naphthyl
13	4-(β-Sulfatoethylsulfonyl)phenyl
14	1-Sulfo-6-carboxy-2-naphthyl
15	2-Sulfophenyl
16	1,5-Disulfo-2-naphthyl
17	3-Amino-7-sulfo-5-naphthol
18	2-Amino-7-sulfo-5-naphthol
19	1-Amino-3,6-disulfo-8-naphthol
20	1-(β-Aminoethyl)-4-methyl-3-carbamoyl-2-hydroxypyrid-6-one
21	1-(β-Aminoethyl)-4-methyl-3-cyano-2-hydroxypyrid-6-one
22	Fluorine
23	Chlorine
24	Red orange
25	Red (498)
26	Yellow
27	Bluish red (545)
28	Scarlet

Example 112

At 0°C and a pH of 4-5 47 parts of the known aminodiazo compound of the formula



is reacted in 300 parts water with 8 parts cyanuric fluoride. The resulting product is then reacted with 38 parts 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline at a temperature of 20°C and a pH value between 5 and 6. The reaction is stopped after 4 h. The dye in accordance with the invention is isolated from the synthesis solution by evaporation or spray drying. The electrolyte-containing dye powder of the alkali metal salt of the diazo compound

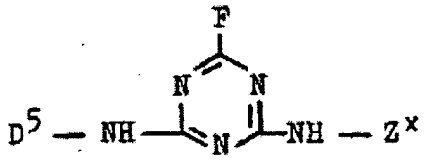


(λ_{max} = 470 nm)

with Z^x having the above meaning is obtained; it dyes cotton reddish brown fast shades.

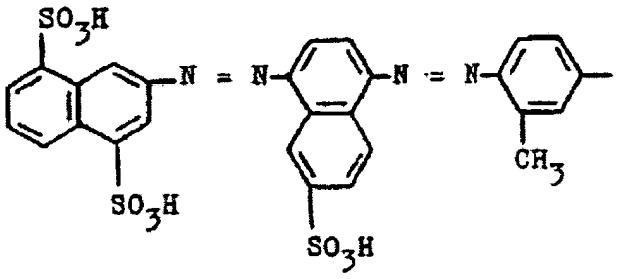
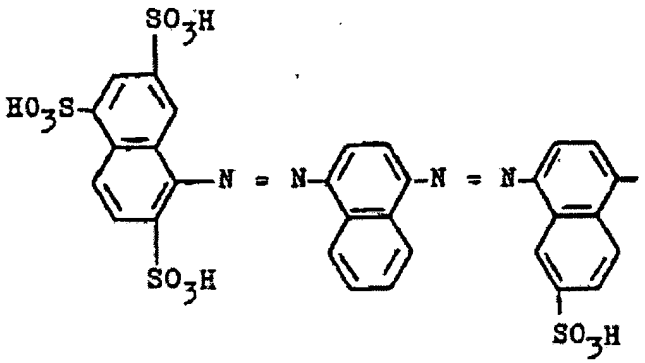
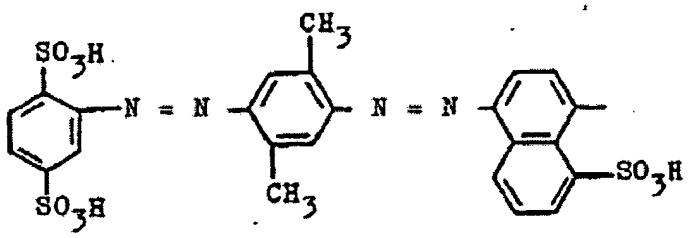
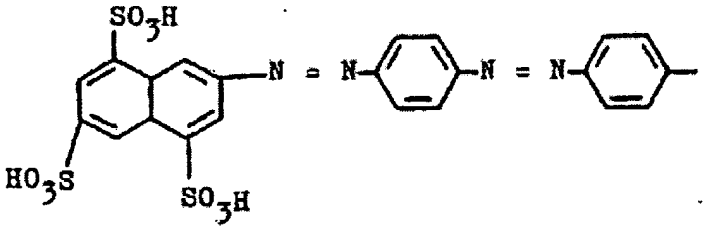
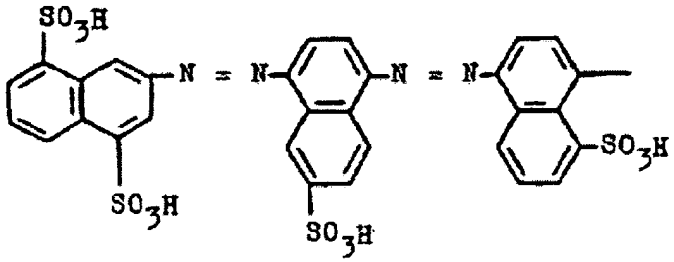
Examples 113-117

Other dyes in accordance with the invention in correspondence with the general formula (F)



(F)

are described with the aid of these components in the following table examples, where Z^x stands for the fiber reactive residue of the previously given general formula (25). These dyes in accordance with the invention can be prepared in a manner in accordance with the invention, for example by analogy with Embodiment Example 112, by the reaction of the starting amino diazo dye that can be seen from the residue D^5 given in the relevant table example, which corresponds to the general formula D^5-NH_2, with cyanuric fluoride and compound 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline. They likewise have very good fiber reactive dye properties and dye cellulose fiber materials in particular the strong true shades that are listed for the relevant example.

① Bsp.	② Rest D^5-	③ Farbton
113		braun ④
114		rotbraun ⑤
115		orangebraun ⑥ (453)
116		orangebraun ⑦
117		rotbraun ⑤

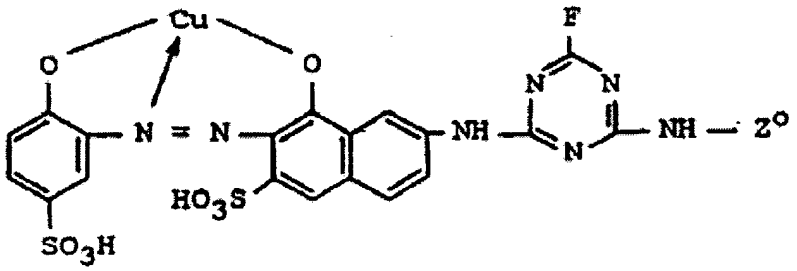
Key: 1 Example

2	Residue D^5-
3	Shade
4	Brown
5	Reddish brown
6	Orange brown (453)
7	Orange brown

Example 118

To a solution of the sodium salt of 18.9 parts 2-aminophenol-4-sulfonic acid in 70 parts water and 90 parts ice is added 7.4 parts 96% sulfuric acid and diazotization is carried out with 14 parts of an aqueous 40% sodium nitrite solution at 0-10°C with stirring for 1 h. The excess nitrite is broken down by means of amidosulfonic acid. A solution of 27.5 parts of the sodium salt of 1-naphthol-7-amino-3-sulfonic acid in 200 parts water is added and the coupling reaction is carried out at a pH kept between 4.5 and 5. Then 25 parts copper(II) sulfate pentahydrate is added, and stirring is continued for an hour at a pH between 5 and 6 and is about 20°C. The reaction batch is mixed with some diatomaceous earth and filtered and the filtrate is slowly mixed with 13.6 parts 2,4,6-trifluoro-1,3,5-triazine (cyanuric fluoride) with thorough stirring, keeping the pH between 4 and 4.5 by means of an aqueous 2n sodium carbonate solution. Then a solution of 65 parts compound 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline is added to the reaction mixture at about 20°C and while maintaining a pH between 5 and 6. The batch is stirred for another 4 h at about 20°C, then filtered after the addition of a little diatomaceous earth and adjusting a pH value of 5, and the compound in accordance with the invention is isolated by evaporation or spray drying the filtrate.

The alkali metal salt of the copper complex monoazo dye of the formula



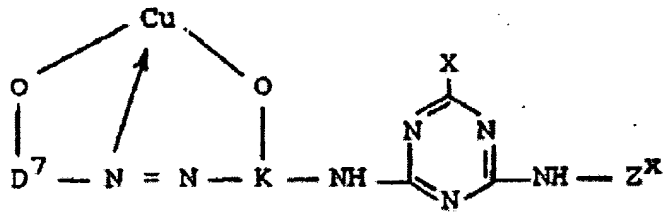
(λ_{max} = 525 nm)

with Z^x having the above meaning, is obtained as an electrolyte salt-containing powder. The dye in accordance with the invention produces red-violet dyeings with high color intensity,

good color yield and good fastness by the conventional application and fixing methods for fiber reactive dyes such as the well-known exhaustion and padding processes on wool or synthetic polyamide fibers and especially on cellulose fibers; of the types of fastness the good washing fastness, good lightfastness and good perspiration fastness should be noted.

Examples 119-132

Other dyes in accordance with the invention corresponding to a general formula (G)



(G)

with Z^x having the meaning given above, are described by means of their components in the following table examples. They can be prepared in the manner in accordance with the invention, for example by analogy with the data in Embodiment Example 119, by reacting the components that are evident from the formula, like the phenol or naphthol diazo component in correspondence with the general formula HO-D7-NH_2, the amino group-containing coupling component H-K(OH)-NH_2, cyanuric fluoride or cyanuric chloride, and 3,5-bis[γ-(β'-sulfatoethylsulfonyl)propylaminocarbonyl]aniline and on the materials indicated in the description, especially cellulose fiber materials, they produce strong and fast dyeings in the shades indicated in the table, by the usual dyeing methods for fiber reactive dyes.

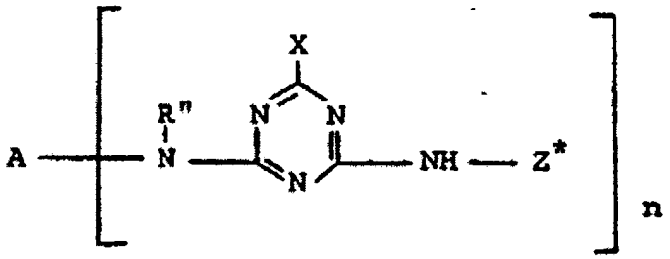
(1) Bsp.	(2) Diazokomponente $HO-D^7-NH_2$	(3) Kupplungskomponente $H-K(OH)-NH_2$	(4) Rest X	(5) Farbton
119	(6) 4-(β-Sulfatoethylsulfonyl)-2-aminophenol	3-Sulfo-6-amino-1-naphthol (17)	(23) Fluor	violett (24)
120	(7) 5-(β-Sulfatoethylsulfonyl)-4-methoxy-2-aminophenol	3,6-Disulfo-1-amino-8-naphthol (18)	Fluor	blau (26)
121	(8) 5-(β-Sulfatoethylsulfonyl)-2-amino-phenol	4,6-Disulfo-1-amino-8-naphthol (19)	Fluor	violett
122	(9) 5-Sulfo-2-aminophenol	dito	Chlor (25)	violett
123	(10) 4-(β-Sulfatoethylsulfonyl)-2-aminophenol	3-Sulfo-7-amino-1-naphthol (20)	Fluor	violett
124	(11) 5-Sulfo-4-methoxy-2-aminophenol (18)	3,6-Disulfo-1-amino-8-naphthol (18)	Fluor	blau
125	(12) 8-(β-Sulfatoethylsulfonyl)-6-sulfo-2-amino-1-naphthol	dito	Chlor	blau
126	(13) 6,8-Disulfo-2-amino-1-naphthol	dito	Chlor	blau
127	(14) 4-Sulfo-2-aminophenol	3-Sulfo-6-amino-1-naphthol (17)	Fluor	violett
128	(15) dito	3,6-Disulfo-1-amino-8-naphthol (18)	Fluor	violett
129	dito	1-(2'-Sulfo-4'-aminophenyl)-3-methyl-5-pyrazolon (21)	Fluor	rotstichig braun (27)
130	dito	1-(2'-Sulfo-4'-aminophenyl)-3-carboxy-5-pyrazolon (22)	Fluor	dito
131	(16) 4,6-Disulfo-2-aminophenol	dito	Chlor	dito
132	(9) 5-Sulfo-2-aminophenol	3,6-Disulfo-1-amino-8-naphthol (18)	Fluor	violett

Key:
1 Example
2 Diazo component $HO-D^7-NH_2$
3 Coupling component $H-K(OH)-NH_2$
4 Residue X
5 Shade
6 4-(β-Sulfatoethylsulfonyl)-2-aminophenol
7 5-(β-Sulfatoethylsulfonyl)-4-methoxy-2-aminophenol
8 5-(β-Sulfatoethylsulfonyl)-2-aminophenol
9 5-Sulfo-2-aminophenol
10 4-(β-Sulfatoethylsulfonyl)-2-aminophenol
11 5-Sulfo-4-methoxy-2-aminophenol
12 8-(β-Sulfatoethylsulfonyl)-6-sulfo-2-amino-1-naphthol
13 6,8-Disulfo-2-amino-1-naphthol
14 4-Sulfo-2-aminophenol
15 ditto
16 4,6-Disulfo-2-aminophenol
17 3-Sulfo-6-amino-1-naphthol
18 3,6-Disulfo-1-amino-8-naphthol
19 4,6-Disulfo-1-amino-8-naphthol
20 3-Sulfo-7-amino-1-naphthol
21 1-(2'-Sulfo-4'-aminophenyl)-3-methyl-5-pyrazolone

22 1-(2'-Sulfo-4'-aminophenyl)-3-carboxy-5-pyrazolone
23 Fluorine
24 Chlorine
25 Violet
26 Blue
27 Reddish brown

Claims

1. A compound that corresponds to the general formula (1)



(1)

in which:

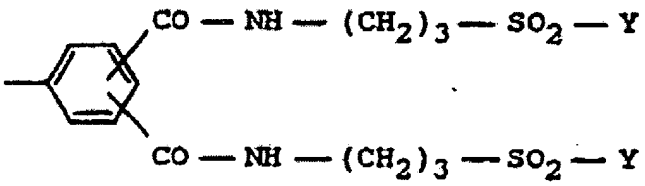
A is the residue of a sulfo group-containing dye;

n is the number 1 or 2, preferably 1;

R" is a hydrogen atom or an alkyl group with 1-4 C atoms;

X is a chlorine or fluorine atom;

Z* is a group of the general formula (2)



(2)

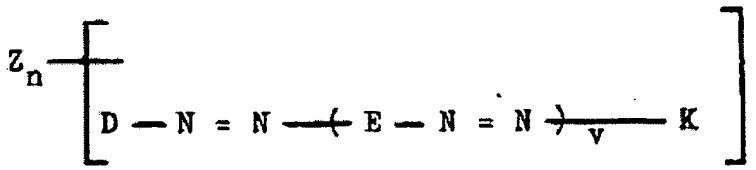
in which

Y is the vinyl group or the β-chloroethyl, β-phosphatoethyl or the β-acetyloxyethyl group or preferably the β-sulfatoethyl group.

2. A compound as in Claim 1, which is characterized by the fact that A is the residue of a sulfo group-containing mono- or diazo dye.

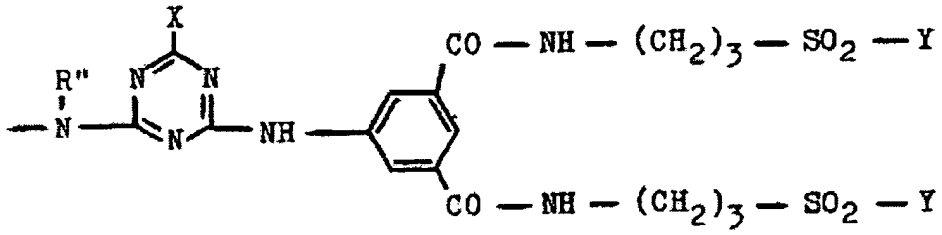
3. A compound as in Claim 1 or 2, which is characterized by the fact that R" is hydrogen and Y is β-sulfatoethyl.

4. A compound as in Claim 1 corresponding to the general formula (4a)



(4a)

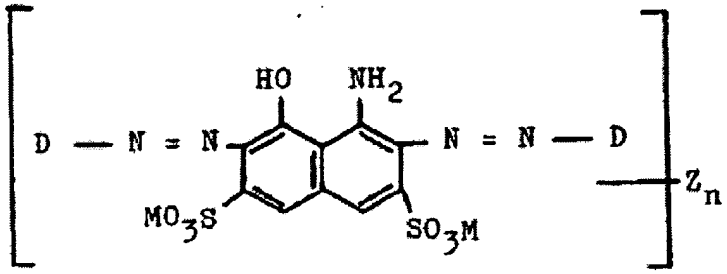
in which D stands for the residue of a diazo component, E is the divalent residue of a compound capable of coupling and diazotization and K is the residue of a coupling component, v is the number 0 or 1, n is the number 1 or 2, and Z is a residue of general formula (3)



(3)

in which X, R" and Y have the meanings given in Claim 1 or 3, where the residue Z is bonded to the residue D or the residue K or in the case n = 2 to D and K each or to both Ds.

5. A compound as in Claim 1 corresponding to the general formula (4b)



(4b)

in which

M is a hydrogen atom or an alkali metal,

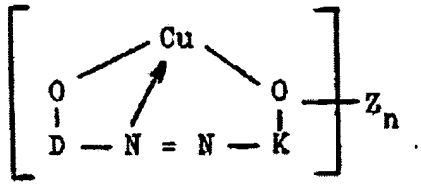
D each stands for the residue of a diazo component, which can have the same meanings or different meanings from each other,

Z is a residue of general formula (3) that is defined and named in Claim 4,

n is the number 1 or 2 and

the residue Z is bonded to the residue D or, in the case n = 2, to both Ds.

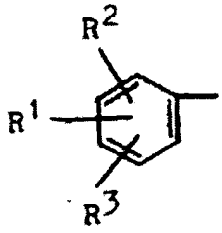
6. A compound as in Claim 1 corresponding to the general formula (4c)



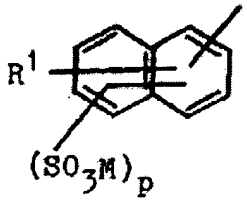
(4c)

in which D stands for the residue of a diazo component, K means the residue of a coupling component, Z means a residue of the general formula (3) defined and named in Claim 4, n is the number 1 or 2, preferably 1, and the residue Z is bonded to the residue D or the residue K or in the case n = 2 to each of D and K.

7. A compound as in Claim 4, which is characterized by the fact that n stands for the number 1 and Z is bonded to K and D is a residue of the general formula



Or



in which

R^1 is a hydrogen atom, a sulfo group or a group of the general formula $-SO_2-Y$, with Y having the meaning in Claim 1,

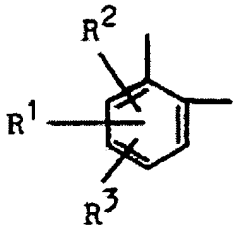
R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, cyano, carboxy, sulfo, alkanoylamino with 2-5 C atoms, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, nitro, sulfamoyl, N-(C_1-C_4 alkyl) sulfamoyl, alkylsulfonyl with 1-4 C atoms, phenylsulfonyl or phenoxy,

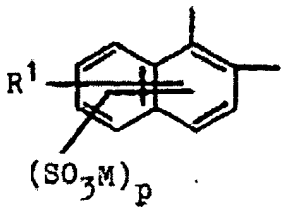
p is the number 0, 1 or 2 and

M is a hydrogen atom or an alkali metal.

8. A compound as in Claim 6, which is characterized by the fact that n stands for the number 1 and Z is bonded to K and D is a residue of the general formula



Or



in which

R^1 is a hydrogen atom, a sulfo group or a group with the general formula $-SO_2-Y$, with Y having the meaning given in Claim 1,

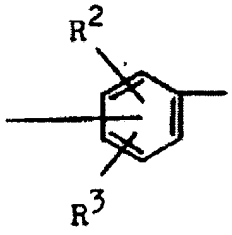
R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, cyano, carboxy, sulfo, alkanoylamino with 2-5 C atoms, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, nitro, sulfamoyl, N-(C_1-C_4 alkyl) sulfamoyl, alkylsulfonyl with 1-4 C atoms, phenylsulfonyl or phenoxy,

p is the number 0, 1 or 2 and

M is a hydrogen atom or an alkali metal.

9. A compound as in Claim 4, which is characterized by the fact that n stands for the number 1 and Z is bonded to D and D is a phenylene residue of the general formula

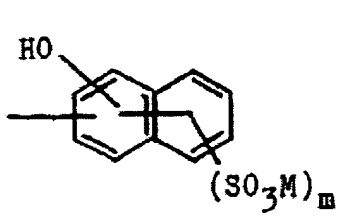


in which

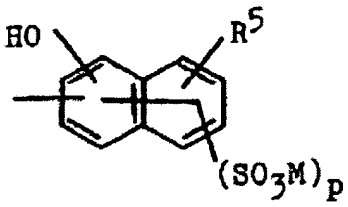
R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, cyano, carboxy, sulfo, alkanoylamino with 2-5 C atoms, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, nitro, sulfamoyl, N-(C_1-C_4 alkyl) sulfamoyl, alkylsulfonyl with 1-4 C atoms, phenylsulfonyl or phenoxy.

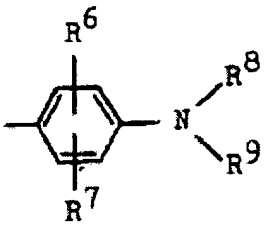
10. A compound as in Claim 4 or 9, which is characterized by the fact that n stands for the number 1, Z is bonded to D and K is a residue of the general formula



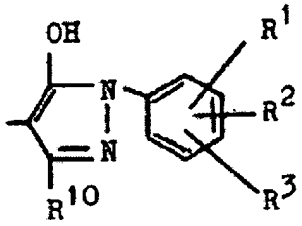
Or



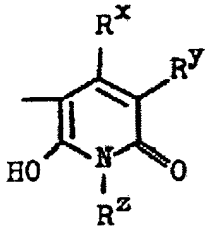
Or



oder



oder



in which

R^1, R^2, R^3, p and M have the meanings given in Claim 7,

R^5 is alkylureido with alkyl groups having 1-6 C atoms, phenylureido, phenylureido substituted in the phenyl residue by chlorine, methyl, methoxy, nitro, sulfo and/or carboxy, alkanoylamino with 2-7 C atoms, cyclohexanoylamino, benzoylamino or benzoylamino substituted in the benzene residue by chlorine, methyl, methoxy, nitro, sulfo and/or carboxy,

R^6 is hydrogen, alkyl with 1-4 C atoms, alkoxy with 1-4 C atoms, bromine, chlorine or alkanoylamino with 2-7 C atoms,

R^7 is hydrogen, alkyl with 1-4 C atoms, alkoxy with 1-4 C atoms, chlorine, alkanoylamino with 2-7 C atoms, ureido or phenylureido,

R^8 is hydrogen or alkyl with 1-4 C atoms, which can be substituted by hydroxy, cyano, carboxy, sulfo, sulfato, methoxycarbonyl, ethoxycarbonyl or acetoxy,

R^9 stands for alkyl with 1-4 C atoms, which can be substituted by hydroxy, cyano, carboxy, sulfo, sulfato, methoxycarbonyl, ethoxycarbonyl or acetoxy, or is benzyl or phenyl or phenyl substituted by alkyl with 1-4 C atoms, alkoxy with 1-4 C atoms, chlorine and/or sulfo,

R^{10} stands for hydrogen, alkyl with 1-4 C atoms, cyano, carboxy, carbalkoxy with 2-5 C atoms, carbonamido or phenyl,

R^x is hydrogen, alkyl with 1-4 C atoms or alkyl with 1-4 C atoms substituted by alkoxy with 1-4 C atoms or cyano,

R^y is hydrogen, sulfo, sulfoalkyl with an alkyl residue having 1-4 C atoms, cyano or carbamoyl,

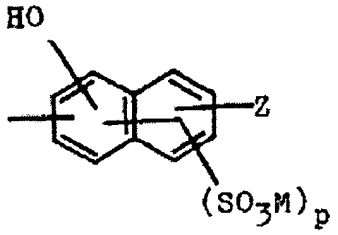
R^z is hydrogen or alkyl with 1-6 C atoms, preferably 1-4 C atoms, which can be substituted by phenyl, sulfo or sulfophenyl,

m stands for the number zero, 1, 2 or 3,

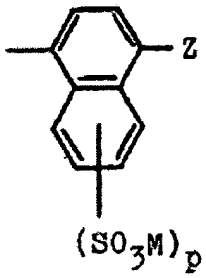
p stands for the number zero, 1 or 2 and

M is a hydrogen atom or an alkali metal.

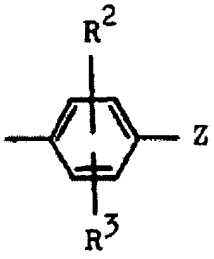
11. A compound as in Claim 4 or 7, which is characterized by the fact that n stands for the number 1, the residue Z is bound to K and the group –K-Z is a residue of the formula



Or

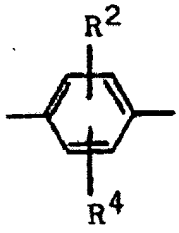


Or

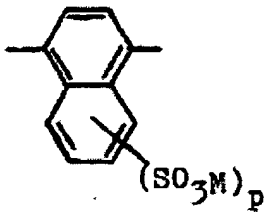


in which R^2 is hydrogen, methyl, methoxy, chlorine, carboxy or sulfo, R^3 is hydrogen, methyl, methoxy, chlorine, carboxy, sulfo or acetylamino, p is the number zero, 1 or 2 and M is hydrogen or an alkali metal and Z has the meaning given in Claim 4.

12. A compound as in at least one of Claims 4, 6, 7 and 9-11, which is characterized by the fact that v stands for the number 1 and E is a residue of the formula



Or



in which

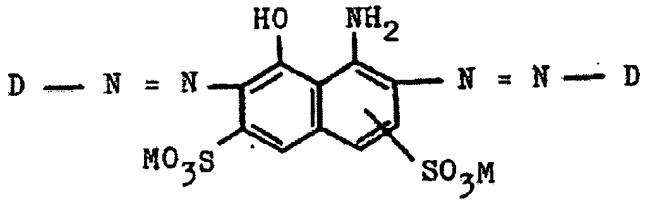
R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^4 is hydrogen, alkyl with 1-4 C atoms, alkoxy with 1-4 C atoms, chlorine, alkanoylamino with 2-5 C atoms, benzoylamino, ureido, phenylureido, alkylureido with 1-4 C atoms in the alkyl residue, phenylsulfonyl or alkylsulfonyl with 1-4 C atoms,

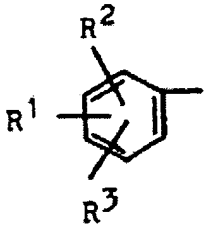
p stands for the number zero, 1 or 2 and

M is a hydrogen atom or an alkali metal.

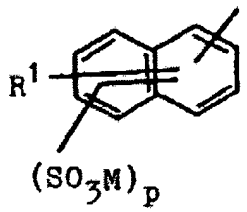
13. A compound as in Claim 5 corresponding to the general formula



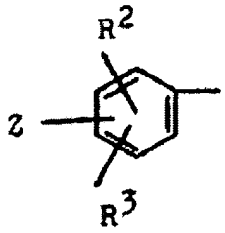
in which both Ds are the same or have different meanings and each is a residue of a general formula



Or



Or



in which

R^1 is a hydrogen atom, a sulfo group or a group with the general formula $-SO_2-Y$, with Y having the meaning given in Claim 1,

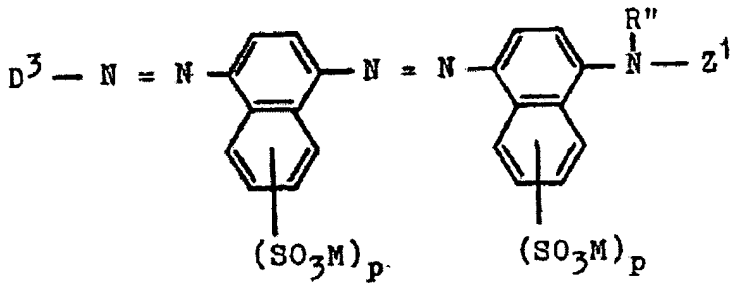
R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, cyano, carboxy, sulfo, alkanoylamino with 2-5 C atoms, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, nitro, sulfamoyl, N-(C_1-C_4 alkyl) sulfamoyl, alkylsulfonyl with 1-4 C atoms, phenylsulfonyl or phenoxy,

p is the number zero, 1 or 2 and

M is a hydrogen atom or an alkali metal, where at least one D is a residue with the fiber reactive group 2 defined and specified in Claim 4.

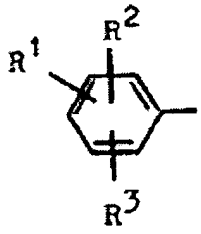
14. A compound as in Claim 1 or 3 of general formula (16a)



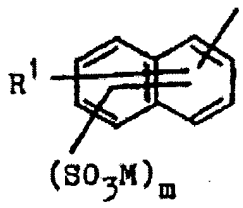
(16a)

in which

D^3 is a residue of the general formula



Or



in which

R^1 is a hydrogen atom, a sulfo group or a group with the general formula $-SO_2-Y$, with Y having the meaning given in Claim 1,

R^2 is hydrogen, methyl, ethyl, methoxy, ethoxy, alkanoyl with 2-5 C atoms, cyano, carboxy, sulfo, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl, fluorine, chlorine, bromine or trifluoromethyl,

R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, cyano, carboxy, sulfo, alkanoylamino with 2-5 C atoms, alkoxycarbonyl with 2-5 C atoms, carbamoyl, N-(C_1-C_4 alkyl) carbamoyl,

fluorine, chlorine, nitro, sulfamoyl, N-(C_1-C_4 alkyl) sulfamoyl, alkylsulfonyl with 1-4 C atoms, phenylsulfonyl or phenoxy,

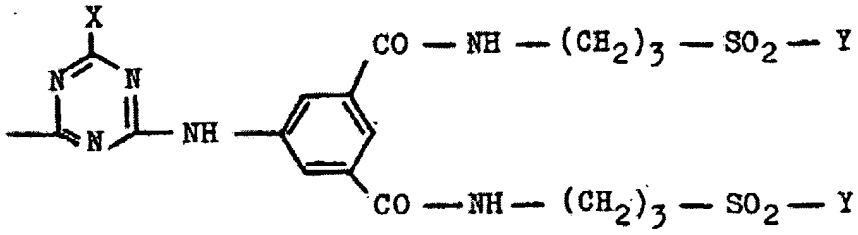
m is the number zero, 1, 2 or 3 and

M is a hydrogen atom or an alkali metal,

R" has the meaning given in Claim 1 or 3,

p stands for the number zero, 1 or 2 and

Z^1 is a residue of the general formula (3a)



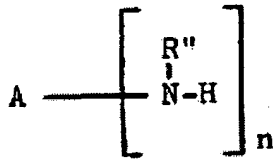
(3a)

with X and Y having the meaning given in Claim 1 or 3.

15. A compound as in at least one of Claims 1-12, which is characterized by the fact that Y stands for the β-sulfatoethyl group.

16. A method for producing the compounds of general formula (1) that are defined and specified in Claim 1, which is characterized by the fact that the usual precursors for water soluble dyes, of which at least one contains a group of the general formula (3) are reacted with each other in the usual procedure to form the corresponding dye,

or by reacting cyanuric fluoride or cyanuric chloride with an amino compound of the general formula (18)



(18)

in which A, R" and n have the meanings given in Claim 1, and an amino compound of the general formula (19)

H_2N-Z* (19)

in which Z* has the meaning given in Claim 1, in any order, by analogy with known procedures for such condensation reactions of cyanuric halides with amino compounds.

17. The use of a compound corresponding to formula (1) from at least one of Claims 1-16 for dyeing and printing hydroxy- and/or carbonamide group-containing material, especially fiber material.

18. A method for coloring (dyeing, including printing) hydroxy and/or carbonamide group-containing material, preferably fiber material, in which a dye is applied to the material or the material or is introduced into the material and the dye is fixed on or in the material by means of heat or with the aid of an alkaline agent or by means of heat and with the aid of an alkaline agent, which is characterized by the fact that a compound corresponding to general formula (1) from at least one of Claims 1-16 is used as dye.

European Patent Office

Application Number EP 90 10 3874

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl[5])
A	EP-A-0 284 568 (CIBA-GEIGY) * Claims 1,2,17 * ---	1	C 09 B 62/04 C 09 B 62/503 D 06 P 1/38
A	EP-A-0 260 227 (CIBA-GEIGY) * Page 9, line 50 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.[5])
			C 09 B
The present search report has been drawn up for all claims.			

Place of search	Date of completion of the search	Examiner
THE HAGUE	May 30, 1990	GINESTET M.E.J.

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.
Y: Particularly relevant if combined with another document of the same category.
A: Technological background.
O: Non-written disclosure.
P: Intermediate document.

T: Theory or principle underlying the invention.
E: Earlier patent document, but published on, or after the filing date.
D: Document cited in the application.
L: Document cited for other reasons.

.....

&: Member of the same patent family, corresponding document.